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SURFACE CARBON CHEMISTRY AND GRAIN SIZE
OF 18-4-1 HIGH SPEED STEEL

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Abstract

Data are presented which show the relationship of time, temperature and furnace atmospheres to chemical changes which take place on the surface of 18-4-1 high speed steel during its heat treatment. These data apply, to a limited degree, to several special methods of heat treatment. The microstructures resulting from chemical changes on the surface were studied and photomicrographs are included to show the effect of these changes on structure.

A study of grain size was made in conjunction with the study of surface carbon chemistry. The effects of time, temperature and heat treating atmospheres upon the resulting grain size of this steel were studied in a quantitative manner.

INTRODUCTION

HIGH speed steel is a material used essentially for the manufacture of cutting tools, particularly those tools used in the metal industry. The heat treatment of these tools is a most important step in their manufacture. Since the years 1898-1900, when Messrs. Taylor and White (1)[1] first discovered the benefits of high temperature treatments, until the present day, numerous investigations and researches have been made to determine the most useful properties of high speed steels. Many of these articles deal with heat treatment, and frequently reference is made to decarburization; occasionally carburization is mentioned. None of the articles, to the best of the author's knowledge, specifically mention the chemical changes that take place on the surface under various heat treating conditions.

The life or usefulness of practically all tools is determined to a great extent by their surface condition. Since the surface of the tools, or the immediate vicinity thereto, is of such importance, it was decided that a study of the interaction between the heat treating fur-

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[1] The figures appearing in parentheses pertain to the references appended to this paper.

nace atmospheres and the surface of the steel, especially with regard to carburization or decarburization, offered a fertile and practical field for investigation.

A direct corollary to the study of surface carbon chemistry was an investigation of grain growth. The problem of grain growth in high speed steel has and will continue to receive considerable attention. Today the majority of tools made from high speed steel are treated from a temperature range of 2300 to 2350 degrees Fahr. (1260 to 1290 degrees Cent.). In leading commercial catalogs, technical papers and text books, the usual instructions are to hold the tools in the superheat only long enough to reach furnace temperature. Should the tools remain in the furnace a few minutes longer than the time required to bring them to furnace temperature, we are told that considerable grain growth will occur.

The effect of furnace atmosphere upon grain growth (2), (3), (4) has been given a great deal of attention during the past few years, and several articles have appeared which treat this subject at considerable length. Since the results obtained on grain growth during the study of surface carbon chemistry were found to be at variance with a great deal of the published data, they are included.

CONDITIONS OF INVESTIGATION

Today there are approximately eighteen distinct types of high speed steel available. This number is exclusive of the various brands. Of the eighteen types, the one generally known as 18-4-1 (18.00 per cent tungsten, 4.00 per cent chromium, 1.00 per cent vanadium) has a great diversity of uses and has found the greatest favor in the trade. The author would estimate that approximately 80 per cent of the high speed tools in use are made from 18-4-1 type steel. In view of the numerous uses for which this steel is employed, this investigation is confined to this class of material. Further, the 18-4-1 high speed steel used in this work was melted in a high frequency coreless induction furnace.

Since the primary purpose of this paper relates to surface carbon chemistry during its heat treatment and the resultant grain size, the various steps of manufacture will not be discussed. In passing it may be well to mention that, as in all high quality tool steels, each and every operation is carefully controlled.

A necessary prerequisite to the study of surface carbon chemistry is the proper preparation of test sections. It is recognized that bar stock may contain surface conditions which might influence final results, and because of this possibility, all test sections were machined, removing sufficient material in each instance to eliminate questionable results which might have been caused by bar condition. Carbon is influenced more than any other of the elements during manufacture, consequently the surfaces of the machined bars were analyzed for this element. The results of these analyses were checked against the original carbons of the melt to insure the elimination of bar surface condition. Round sections were used because they offered an easy means for the preparation of samples for chemical analysis. In addition, several designs were used to simulate conditions encountered in tools.

The greater portion of the heat treating was done from an electrically heated furnace which had a controlled atmosphere and automatic temperature control. This furnace was an ideal piece of equipment for this type of work, since the atmospheres could be varied over wide ranges without affecting the temperatures.

The gas employed for controlling atmospheres was bottled propane, the analysis of which follows:

		Per Cent
Ethane	C_2H_6	2
Propylene	C_3H_7	19
Propane	C_3H_8	76
Butylene	C_4H_8	1.5
Butane	C_4H_{10}	
Iso Butane	C_4H_{10}	1.5
Iso Pentane	C_5H_{12}	

Several tests were made from a gas-fired furnace, heated with by-product coke oven gas, having an analysis of:

	Per Cent
CO_2	1.8
Illuminants	3.3
O_2	0.3
CO	8.5
CH_4	24.7
H_2	51.0
N_2	Balance

This gas-fired furnace was equipped with a gas-air mixer, and after the atmosphere was adjusted, the temperature could be regulated without any appreciable change in the atmosphere. The prod-

ucts of combustion were the only means for controlling the atmospheres in this furnace.

The third type furnace was oil-fired. The analysis of the oil was unknown, but was of the commercial type usually used in industrial heating.

In addition to the tests treated in the previously mentioned equipment, samples were submitted to a number of firms for hardening. The types of gas used by these firms for controlling furnace atmospheres are included in the data submitted by them.

A study of surface carbon chemistry during heat treatment requires some knowledge of furnace atmosphere. Throughout the work, the furnace atmospheres were analyzed for CO_2, O_2 and CO with a modified Orsat gas apparatus. The CO_2 was absorbed in a solution of potassium hydroxide (KOH) which had a specific gravity of 1.55. The O_2 was absorbed with pyrogallon. This solution consisted of 15 gr. pyrogallic acid dissolved in 10 cc. of H_2O (hot) which was later added to 100 cc. KOH (sp. gr. 1.55). The CO was analyzed with a solution known commercially as Cosorbent.

Furnace atmospheres contain gases other than the three mentioned, namely, nitrogen, hydrogen, moisture (H_2O), and possibly several hydrocarbons. Naturally when running an oxidizing atmosphere, the hydrogen and hydrocarbons are absent.

A section of this paper deals with grain size as influenced by furnace atmosphere, time and temperature. The grain size in hardening any steel is dependent primarily upon time and temperature; consequently in an investigation of this type, it is important to be positive that the temperatures are reasonably correct. The temperatures in the electric furnace were controlled with a platinum, platinum-rhodium thermocouple, and temperature records were obtained with a recording potentiometer. Chromel-alumel thermocouples were used to obtain the temperatures of both gas- and oil-fired furnaces. The temperatures in these two furnaces were controlled with an indicating potentiometer. The potentiometers on each of the three furnaces were carefully balanced prior to each test. In addition to the temperatures obtained with the pyrometers for each of these furnaces, they were frequently checked with two portable checking instruments, a millivoltmeter* and a wall type indicator with a temperature range of 700 to 2500 degrees Fahr. (370 to 1370 degrees Cent.).

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* L. & N. Model C.

After the specimens were machined, they were carefully cleaned in gasoline, to remove any grease or oil which might have influenced final results, and then handled with clean canvas gloves. The samples were placed in the preheat and transferred from the preheat to the high speed furnace with a pair of tongs burned free of grease or oil.

A stop-watch was used to determine the length of time the specimens were in the high heat furnace. The time required for the specimens to reach furnace temperature, except in a few instances, was judged by eye.

All of the samples after being heated under specific conditions of time, temperature and atmosphere were oil-quenched.

The preparation of samples for chemical analysis was a most important step throughout the work. The test sections, after oil quenching were cleaned in gasoline to remove the oil, and placed in a still air electric furnace at a temperature of around 1000 degrees Fahr. (540 degrees Cent.) to burn off the gasoline. When at heat, they were transferred to a lead pot operated at a temperature of approximately 1450 degrees Fahr. (790 degrees Cent.). While the pieces were in the lead, the top of the bath was covered with a generous amount of salt, which adhered to the surface of the sections when withdrawn, and acted as a protective coating during the cooling. The heating for semi-annealing was followed by lime cooling to room temperature; the salt and lime which adhered to the surface were removed with hot water. The samples were given a final cleaning in 1:1 HCl at approximately 160 degrees Fahr., and were in the acid only long enough to remove the oxide film. When acid cleaning is used it is necessary to remove the black smudge which adheres to the surface. This step in sample preparation requires a great deal of care to insure that the samples are pickled white. When properly cleaned, surface turnings of 0.0025 inch on the radius were machined for chemical carbon analysis; usually three cuts were made.

Fracture characteristics and grain size determinations on the as-hardened sections were evaluated by using two recently developed methods. The Shepherd fracture standards (5) were employed for rating fractures. These consist of ten fractures, No. 1 being extremely coarse; No. 10 being very fine; the other numbers lying between these two extremes. The grain size was established by using the intercept method (6), which consists of counting the number of grains intercepted at a magnification of 1000 diameters by

a 5-inch line. The results given for this method of grain size determination are the average of ten separate counts per specimen.

Specimens for both the fracture and the intercept grain count were obtained from a majority of the heat treated samples by removing a disk (immediately after oil quenching) from one end, approximately ½ inch thick. After determining the fracture characteristics, one-half was examined microscopically in the as-hardened condition; the remaining half was examined after tempering at 1050 degrees Fahr. (565 degrees Cent.). The removal of the ½-inch disk, in addition to providing a means for the study of fractures and an examination of structure, served to eliminate any end effect when turnings for chemical carbon analysis were obtained.

DISCUSSION OF RESULTS

There are a number of variables which may be encountered when heat treating high speed steels, and since this paper covers some of these, the data will be more easily presented and more readily followed by dividing the results into two separate parts:

PART I—SURFACE CARBON CHEMISTRY
PART II—GRAIN SIZE

The following subdivisions will be discussed under Part I—Surface Carbon Chemistry:

    1.   The effect of preheating atmospheres.

    2.   The effect of superheating atmospheres in electric, gas and oil-fired furnaces.

    3.   The effect of water quenching.

    4.   The confirmative tests obtained by co-operative firms.

    5.   Microstructures.

    6.   The effects of variable time and variable atmosphere with constant temperature.

    7.   The effect of variable time with constant atmosphere and constant temperature.

    8.   The effect of variable time and variable temperatures and constant atmosphere.

    9.   The effect of atmospheres containing 16 per cent CO or higher.

    10.   Probable curves for time and atmospheres for 2350 degrees Fahr. (1290 degrees Cent.).

11.   The effect of atmospheres on elements other than carbon.

12.   The effect of drawing (tempering) upon carburized zones.

13.   The effect of atmospheres on size and weight change.

14.   Miscellaneous tests, including blind holes, contact surfaces, borax coating, carbon blocks and smith forge treating.

In the discussion of Part II—Grain Size—the results will be classified under the following subdivisions:

1.   Grain size obtained when treating from electric, gas and oil fired furnaces.

2.   Grain size obtained by co-operative firms.

3.   Grain size obtained with variable time, variable atmosphere and constant temperature.

4.   Grain size obtained with variable time, constant temperature and constant atmosphere.

5.   The effect upon grain size of variable time, variable temperature and variable atmospheres.

6.   Grain size on tests with unbalanced sections.

7.   Grain size on bar stock having various cross sectional areas.

8.   The effect of preheating on grain size.

Before proceeding with the discussion of results, all heat treating was done, unless otherwise specified, from a controlled atmosphere electric furnace. The furnaces used by the co-operative firms were of the controlled atmosphere type.

This entire paper deals with 18-4-1 high speed steel, and the analyses of the melts used for the work discussed under the subdivisions are given in Table XXI.

PART I—SURFACE CARBON CHEMISTRY

1.   *The Effect of Preheating Atmospheres*—It is apparently a uniform practice when heat treating high speed steel to preheat the material before placing it into the high heat furnace. The temperatures employed for this phase of the operation usually range between 1500 and 1600 degrees Fahr. (815 and 870 degrees Cent.). It was thought desirable in view of this practice to learn what effect a preheating temperature and several atmospheres had upon surface carbon. The following procedure was employed to study this step in the heat treating operations:

Sections 1-inch round by 3 inches long, machined from $1\frac{1}{4}$-inch round bar stock, were heated to a temperature of 1550 degrees Fahr. (845 degrees Cent.) in a controlled atmosphere electric furnace. The atmospheres ranged from 8 per cent CO to 4 per cent O_2. The pieces were allowed to remain in the furnace for 0.5 hour (approximately 10 minutes at heat). This temperature was not sufficiently high to cause appreciable hardening; consequently the samples were lime cooled. After cooling to room temperature, they were cleaned in 1:1 HCl, and carbon analyses were made. These results are given in Table I. The carbon analysis on the surface of the machined bar

Table I
The Effect of Preheating Atmospheres on Surface Carbon

	Atmosphere		First Cut 0.0000-0.0025"	Carbon Step Down Results — Second Cut 0.0025-0.0050"	Third Cut 0.0050-0.0075"
CO_2	O_2	CO		Per Cent	
8.6	0.0	8.0	0.73	0.73	0.72
9.7	0.0	6.0	0.76	0.74	0.72
11.0	0.0	3.8	0.74	0.73	0.72
12.0	0.0	2.2	0.76	0.74	0.74
13.5	0.0	0.0	0.74	0.73	0.73
12.3	1.9	0.0	0.76	0.74	0.73
10.6	4.0	0.0	0.73	0.72	0.72

Preheating temperature 1550 degrees Fahr.
Specimens 1 inch round by 3 inches long.
Total time in preheat furnace 30 minutes. Lime cooled—cleaned in 1:1 HCl.
Carbon analysis on the machined bar prior to preheating 0.72-0.74 per cent.

prior to preheating was 0.72 to 0.74 per cent. It is apparent from these data, when using this particular type of preheating, that no appreciable change in surface carbon occurred.

2. *The Effect of Superheating Atmospheres in the Electric, Gas- and Oil-Fired Furnaces*—The temperatures most commonly used in heat treating 18-4-1 high speed steel range between 2300 and 2350 degrees Fahr. (1260 and 1290 degrees Cent.). Since these temperatures are so generally used, the investigations in the electric, gas and oil-fired furnaces were conducted at a temperature of 2350 degrees Fahr. (1290 degrees Cent.).

When treating from the electric furnace, specimens were preheated in an atmosphere of 2 per cent CO to a temperature of 1550 degrees Fahr. (845 degrees Cent.) for a total time of 20 minutes. Following the preheat they were superheated to 2350 degrees Fahr. (1290 degrees Cent.) in atmospheres ranging from 15.8 per cent CO to 9.3 per cent O_2. The specimens were allowed to remain in the superheat furnace, regardless of the composition of the atmosphere,

for 5 minutes (approximately 3 minutes to come to heat; 2 minutes at heat). After quenching in oil, chemical samples were prepared as previously described, and surface carbon analyses determined. The results of this test are shown graphically in Fig. 1. Reducing atmos-

Fig. 1—Surface Carbon—Furnace Atmosphere Relationship When Treating from a Controlled Atmosphere Electric Furnace. Specimens 1-Inch Round by 3 Inches Long. Preheated 1550 Degrees Fahr.—2 Per Cent CO Atmosphere—Total Time 20 Minutes. Superheated 2350 Degrees Fahr.—Total Time 5 Minutes.

pheres are represented graphically in terms of per cent CO present; oxidizing atmospheres in terms of per cent O_2. The carbon analysis of the machined bar prior to heat treating was 0.72 per cent. These results were quite surprising in that regardless of the furnace atmosphere, all showed some carburization. It will be noticed that in this test those sections heated in reducing atmospheres showed carburization only on the first step, whereas those treated in oxidizing atmospheres, showed carburization to a depth greater than 0.0075 inch.

The above test was repeated using a 2 per cent O_2 atmosphere in the preheat furnace instead of 2 per cent CO. The superheating time, atmospheres, and temperature were the same as in the previous test. The results of this test are shown in Fig. 2. Again, attention is called to the fact that all samples showed carburization, and as in the previous test, those treated in oxidizing atmospheres showed the greatest degree of carburization.

The results of the above two tests showed that this type of steel carburizes in either reducing or oxidizing atmospheres when oil-quenched from 2350 degrees Fahr. (1290 degrees Cent.). This carburization was independent of the two preheat furnace atmospheres used in these tests.

In view of these results, it was thought desirable to conduct several tests from a gas-fired furnace, since a great deal of heat treating is done with this type of equipment. The range of atmospheres in this furnace was rather limited, since they were controlled with a gas-air mixer which had a narrow range of operation. The furnace employed for these particular tests is commonly referred to
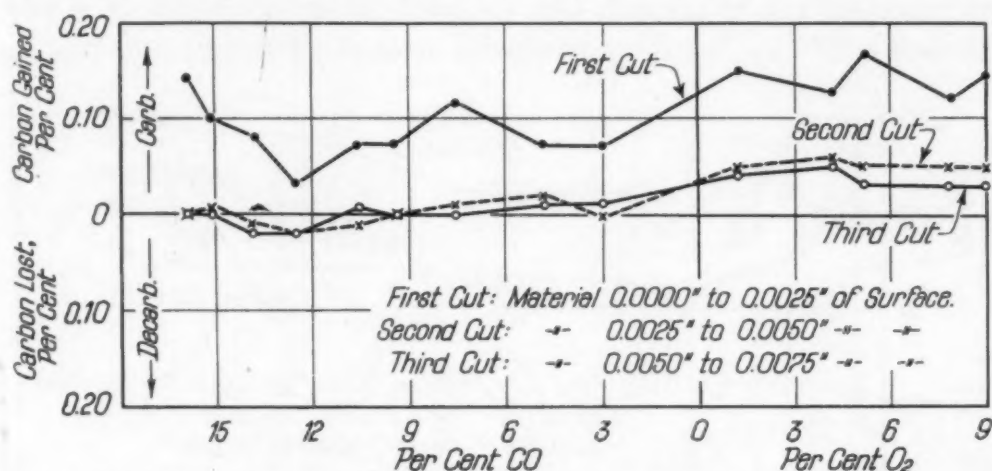

Fig. 2—Surface Carbon—Furnace Atmosphere Relationship When Treating from a Controlled Atmosphere Electric Furnace. Specimens 1-Inch Round by 3 Inches Long. Preheated 1550 Degrees Fahr.—2 Per Cent O_2 Atmosphere—Total Time 20 Minutes. Superheated 2350 Degrees Fahr.—Total Time 5 Minutes.

as a two-high furnace, i.e., the preheating chamber is located directly above the superheating chamber. The exhaust gases from the superheat chamber serves to heat the preheating chamber; consequently, the atmospheres in both were identical.

Four atmospheres were studied, namely, 2.5, 3.0, 6.3 and 7.8 per cent CO. The temperature of the preheating chamber was 1600 degrees Fahr. (870 degrees Cent.); that of the superheating chamber 2350 to 2360 degrees Fahr. (1290 to 1295 degrees Cent.). The samples were in the preheat chamber for a total time of 8 minutes; and in the high heat chamber for a total time of 5 minutes. The analysis of the machined bar prior to treating was 0.72 per cent carbon. The results of this test are shown in Fig. 3. Again, carburization took place, but to a lesser degree than in those tests made in the controlled atmosphere electric furnace.

Finally, to cover the variety of furnaces used in commercial heat treating, several tests were made with an oil-fired furnace. No preheating furnace was available, therefore the samples were placed

directly into the high heat furnace at a temperature of 2350 degrees
Fahr. (1290 degrees Cent.) for a total time of 8 minutes. The
atmospheres ranged from 3.5 per cent CO to 9.8 per cent O_2.
It was found undesirable to operate an oil-fired furnace on the
reducing side for any considerable time because of the large amount
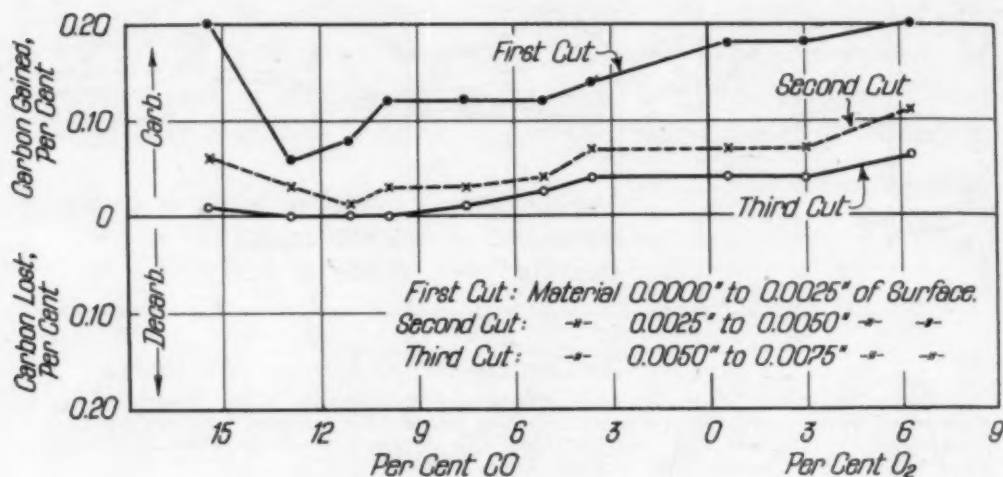of smoke given off by such an atmosphere. Chemical analyses of the

Fig. 3—Surface Carbon—Furnace At-
mosphere Relationship When Treating from
a Gas-Fired Furnace. Specimens 1-Inch
Round by 3 Inches Long—Preheated 1600
Degrees Fahr.—Total Time 8 Minutes. Su-
perheated 2350 Degrees Fahr.—Total Time
5 Minutes. The Atmospheres in the Preheat
Chamber Were Identical to Those in the
Superheating Chamber.

surface carbons of the sections treated from this furnace are shown
in Fig. 4. Again it will be noted that all samples showed carburiza-
tion.

Results of all tests to this point indicated that regardless of type
of furnace or the composition of the furnace atmospheres, some car-
burization took place when using a temperature of 2350 degrees Fahr.
(1290 degrees Cent.). These findings were unexpected and con-
trary to a great deal of the information in the literature.

The question that naturally arises in view of these results is:
"Were the samples for chemical analysis properly prepared?" The
following work was done to check the method of sample preparation:

A section of a machined bar was annealed in lead, handled in the

usual manner, and then analyzed for carbon. The carbon after the
annealing process was exactly the same as in the machined condition.
Several additional samples were put through all operations except
hardening, including machining, cleaning, preheating, lead annealing,
lime cooling, and cleaning in acid. The surface carbon on these sam-
ples checked those of the original bar. Finally, two sets of seven
samples were treated from a temperature of 2350 degrees Fahr.
(1290 degrees Cent.) from seven different atmospheres. Both sets
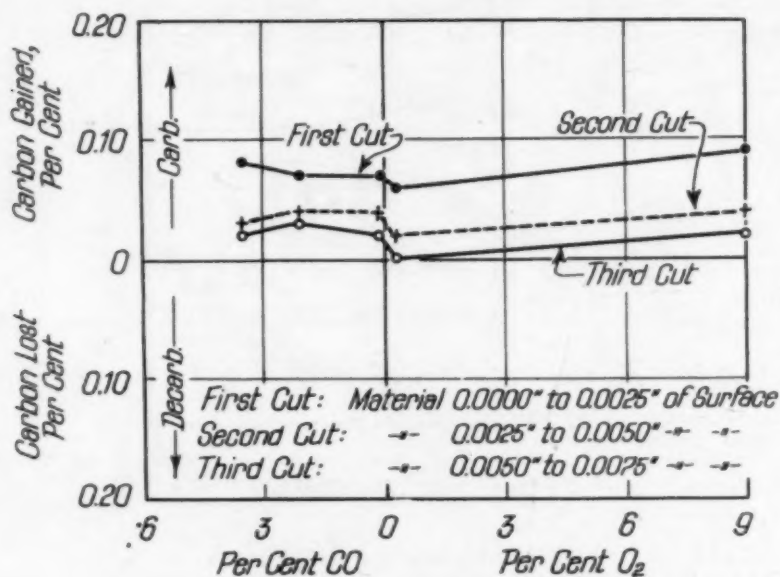
Fig. 4—Surface Carbon—Furnace Atmosphere Relationship
When Treating from an Oil-fired Furnace. Specimens 1-Inch
Round by 3 Inches Long. No Preheat—Superheated 2350 Degrees
Fahr.—Total Time 8 Minutes.

were handled identically up to and including the cleaning in acid.
Surface carbon analyses on one group were made as acid cleaned;
while the second group was polished with No. 0 French emery cloth
to a metallic finish. The amount of material removed when polish-
ing, as determined with a micrometer, was 0.0002 inch on the
diameter. Both sets of samples showed the same degree of carburiza-
tion in the different atmospheres. The check results obtained on sec-
tions after heat treating as described above eliminated questionable
preparation of samples for chemical analysis.

    3. *The Effect of Water Quenching*—All of the foregoing tests
were oil-quenched, and it was thought there was a possibility that this
carburization might be taking place during the oil quench. A group
of specimens 1-inch round by 3 inches long, machined from 1¼-inch

round bar stock, was water quenched from a temperature of 2350 degrees Fahr. (1290 degrees Cent.) in order to determine whether or not this was true. The sections were preheated in a 2 per cent CO atmosphere to a temperature of 1550 degrees Fahr. (845 degrees Cent.) for a total time of 20 minutes, followed by superheating to
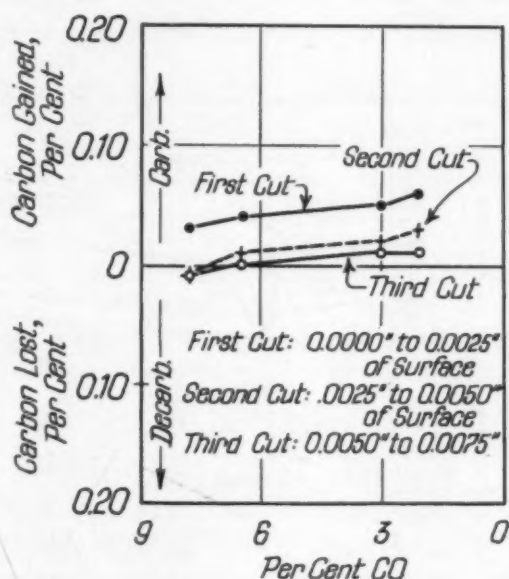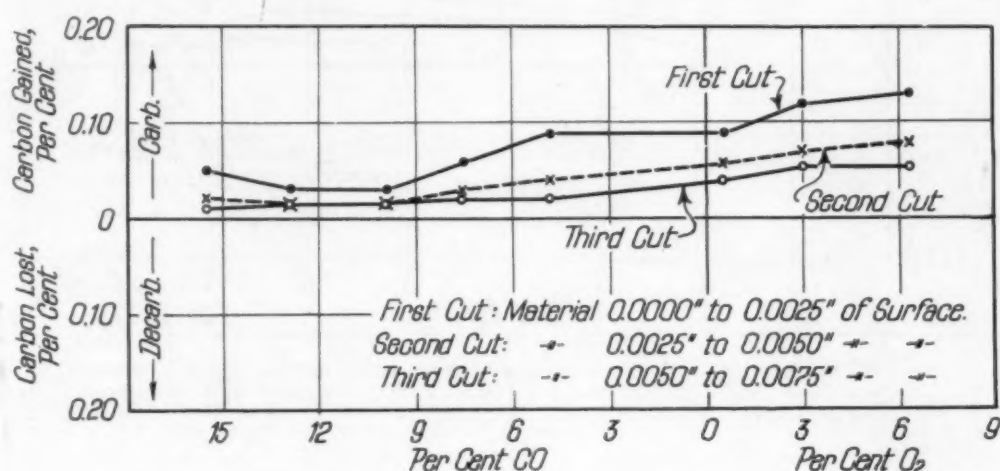

Fig. 5—Surface Carbon—Furnace Atmosphere Relationship When Water-Quenching from 2350 Degrees Fahr. Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr.—2 Per Cent CO Atmosphere—Total Time 20 Minutes. Superheated 2350 Degrees Fahr.—Total Time 5 Minutes.

2350 degrees Fahr. for a total time of 5 minutes. The atmospheres ranged from 15.5 per cent CO to 6.3 per cent O_2. The carbon analysis of the machined bar prior to treating was 0.72 per cent. The temperature of the bath prior to quenching was 150 degrees Fahr., and the samples were allowed to remain in the water until they were black, after which they were air-cooled to room temperature. After annealing and cleaning in the usual manner, surface carbon analyses were made, the results of which are shown in Fig. 5. These data show that all tests carburized regardless of the composition of the furnace atmosphere. Further, as in previous tests, those treated in oxidizing atmospheres showed a greater degree of carburization than those treated under reducing conditions. This water treatment eliminated the oil quench as a possible cause of carburization, and the only remaining alternative is that the carburization takes place during the superheating period.

4. *Confirmative Tests by Co-operative Firms*—The results up to this point were radically different from those anticipated, and as previously mentioned were at variance with some of the published

Fig. 6—Surface Carbon. Furnace Atmosphere Relationship; Heat Treatment by Co-operative Firm "A." Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr.—Total Time 30 Minutes. Superheated 2350 Degrees Fahr.—Total Time 5 Minutes.

data. In view of these unexpected results, it was thought well to ask the co-operation of several firms who commercially heat treat large quantities of high speed steel. The recognized ability of these firms coupled with their many years of heat treating experience served as the most practical check of the foregoing findings. These firms are designated as A, B, C, D and E, and seven samples 1-inch round by 3 inches long, machined from $1\frac{1}{4}$-inch round bar stock, were submitted to each. All tests were machined from the same melt of steel. The firms were requested to preheat the specimens to 1550 degrees Fahr. (845 degrees Cent.) in a 2 per cent CO atmosphere; superheating to 2350 degrees Fahr. (1290 degrees Cent.), using atmospheres of approximately 16.0, 12.0, 8.0 and 4.0 per cent CO, neutral, 3.0 and 6.0 per cent O_2. The time in the superheat furnace was not specified, but it was suggested that all samples, regardless of the composition of the furnace atmosphere, be held for the same length of time.

The fuels used for controlling the furnace atmospheres were:

Firm Designation	Fuel
A	Pyrofax gas (propane)
B	City gas consisting of CO_2 4.5 per cent, O_2 1.7 per cent, illuminants 8.2 per cent, CO 31.3 per cent, CH_4 8.0 per cent, H_2 38.00 per cent, N_2 7.8 per cent.
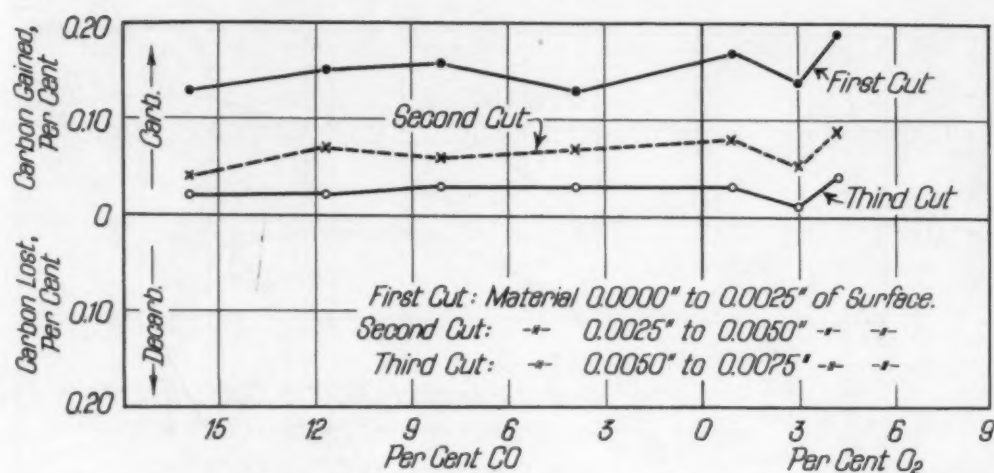
Fig. 7—Surface Carbon—Furnace Atmosphere Relationship; Heat Treatment by Co-operative Firm "B." Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr.—Total Time 20 Minutes. Superheated 2350 Degrees Fahr.—Total Time 4 Minutes.
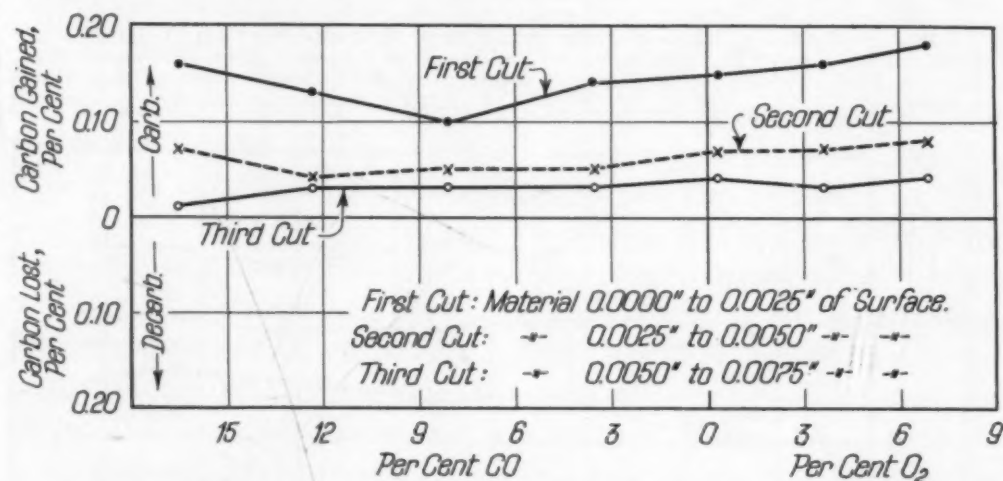
Fig. 8—Surface Carbon—Furnace Atmosphere Relationship; Heat Treatment by Co-operative Firm "C." Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr.—Total Time 22 Minutes. Superheated 2350 Degrees Fahr.—3½ Minutes.

C   City gas CO_2 6.4 per cent, O_2 0.9 per cent, illuminants 9.7 per cent, CO 23.9 per cent, H_2 26.1 per cent, paraffines 11.3 per cent, N_2 21.7 per cent.

D   City gas CO_2 1.3 per cent, O_2 0.6 per cent, illuminants 2.6 per cent, CO 8.8 per cent, H_2 14.2 per cent, N_2 46.5 per cent.

E   Pyrofax gas (propane)

The times used for preheating and superheating were as follows:

Firm	Preheat in Minutes	Superheat in Minutes
A	30	5
B	20	4
C	22*	3½
D	20	5
E	20	5

*Except samples Nos. 3, 4 and 5—which were preheated 25 to 30 minutes.
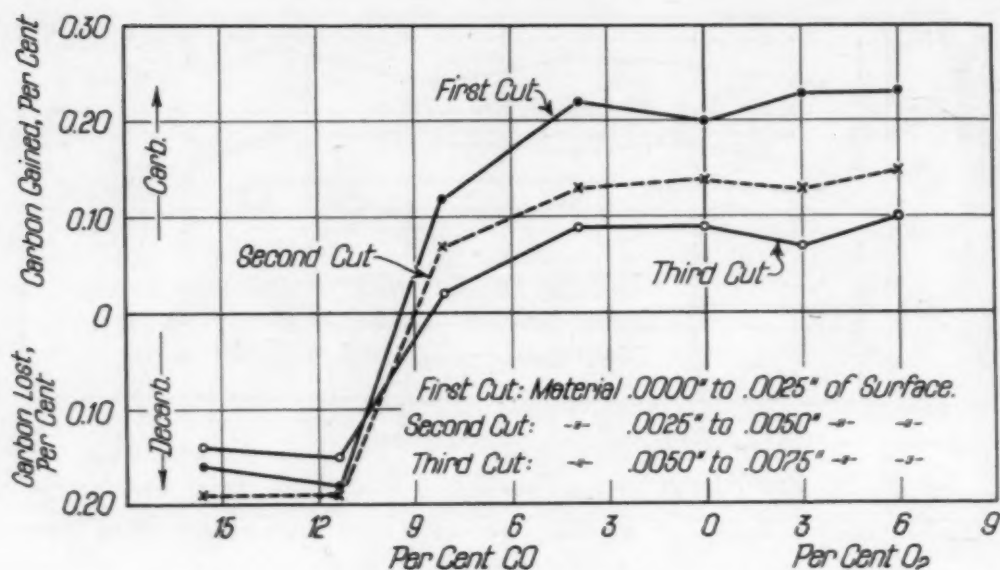
Fig. 9—Surface Carbon—Furnace Atmosphere Relationship; Heat Treatment by Co-operative Firm "D." Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr. Total Time 20 Minutes. Superheated 2350 Degrees Fahr.—Total Time 5 Minutes.
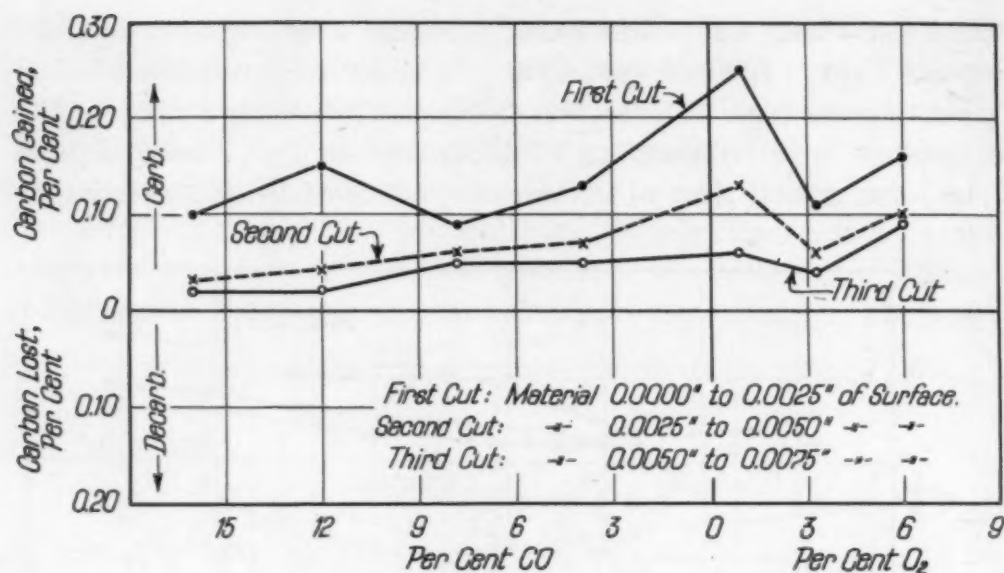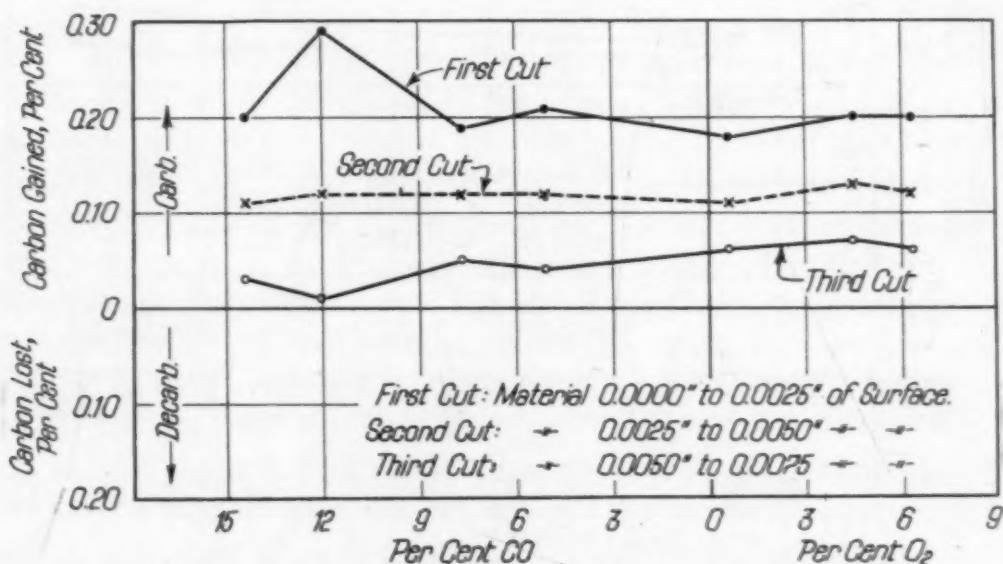

Fig. 10—Surface Carbon—Furnace Atmosphere Relationship; Heat Treatment by Co-operative Firm "E." Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr. Total Time 20 Minutes. Superheated 2350 Degrees Fahr.—Total Time 5 Minutes.

The results of the surface carbon analyses obtained on the samples treated by the different co-operative firms are shown in Figs. 6 to 10 inclusive. These results show that carburization took place regardless of the type of atmosphere, type of fuel used for controlling atmospheres, or the time at the superheat. The only exceptions were
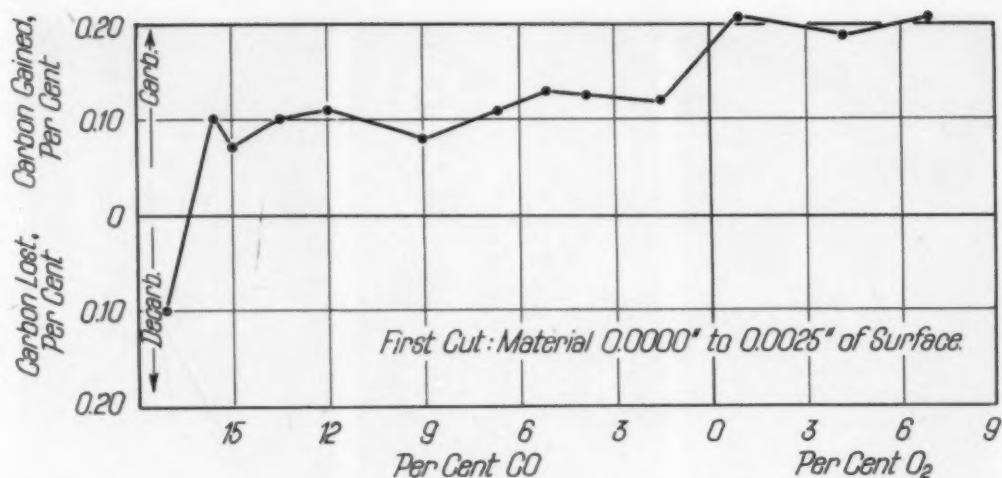
Fig. 11—Composite Curve of all Tests Run to Date Including Those of the Co-operative Firms. All Tests Treated from 2350 Degrees Fahr. The Time in the Super-heating Furnaces Ranged from 3½ to 10 Minutes. Data Plotted Based on the First Cut —0.0000 to 0.0025 Inch.

the two samples treated by Firm D which were superheated in atmospheres of 15.5 and 11.5 per cent CO. The reason these two samples showed decarburization is unknown. Several hundred samples have been treated and analyzed for surface carbon, and of this large number these are the only two which showed decarburization.

Fig. 11 is a composite curve of all of the results obtained to date. This curve is composed of the average results obtained in various type furnaces which were operated with different types of fuel for controlling the atmospheres, and covers tests treated from 2350 degrees Fahr. (1290 degrees Cent.) for 3.5 to 10 minutes. The author is of the opinion that this chart indicates what normally happens when this type of steel is furnace treated at 2350 degrees Fahr. (1290 degrees Cent.) for the usual times, and clearly indicates that some carburization may be expected when the atmospheres are between 15.0 per cent CO and 7.0 per cent O_2.

5. *Microstructures*—All microspecimens were etched in 2 per cent nital prior to examination.

When the carburization is of the magnitude as shown in the foregoing tests, it cannot be seen microscopically in the as-hardened condition. The carburized area can be revealed by tempering from a temperature of 950 to 1100 degrees Fahr. (510 to 595 degrees Cent.). There is a possibility of misinterpreting this carburized zone as decarburization, consequently, attention is called to the three photomicrographs, Figs. 12, 13 and 14.
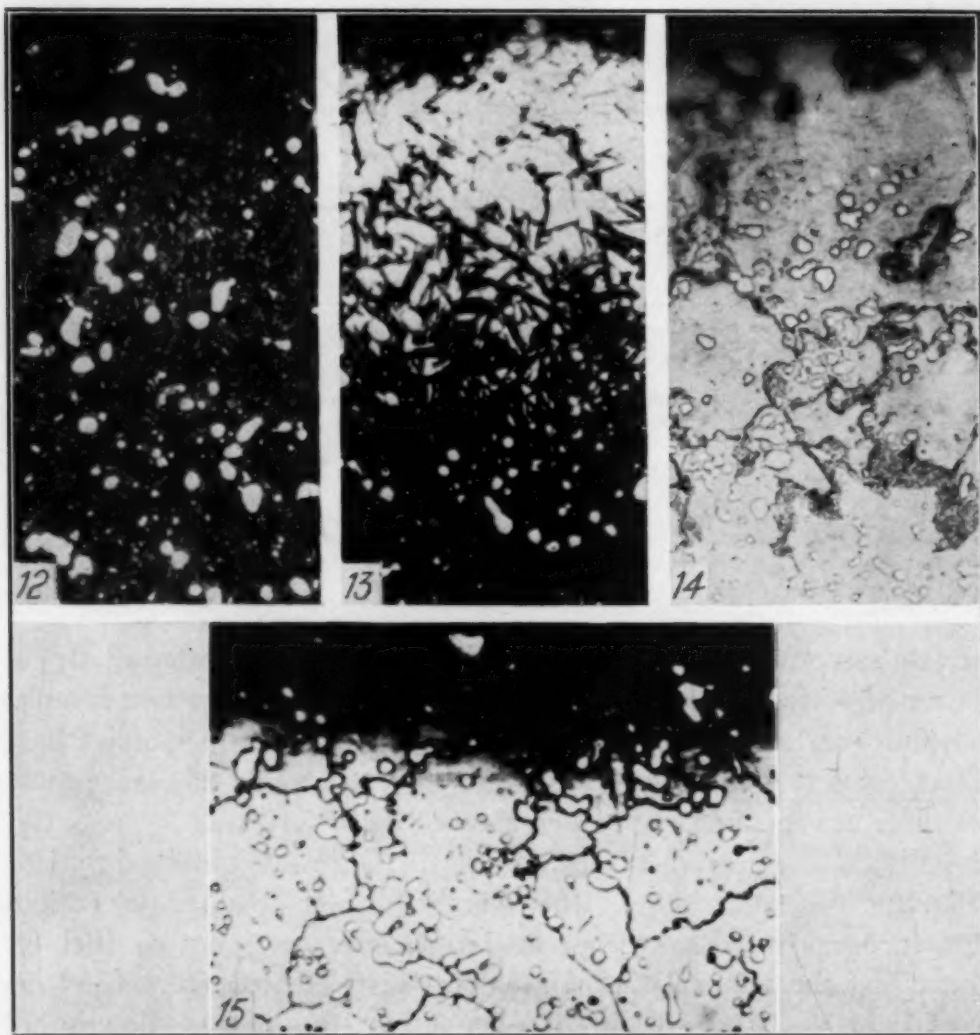
Figs. 12 to 14—Typical Structures (Edge) of Treated 18-4-1 High Speed. Fig. 12 —X-1000 Oil-quenched 2350 Degrees Fahr., Drawn 1050 Degrees Fahr.—Neutral Edge. Fig. 13—X-1000 Oil-quenched 2350 Degrees Fahr., Drawn 1050 Degrees Fahr. Carburized Edge. Fig. 14—X-500 Oil-Quenched 2350 Degrees Fahr., Not Drawn. Decarburized Edge.

Fig. 15—Oil-Treated 2350 Degrees Fahr. Surface Does Not Show Carburized Condition. × 1000.

Decarburization can be seen in the as-hardened, or the as-hardened-and-drawn condition; while carburization as encountered in normal heat treating can be seen only after tempering. The microscope can be used to estimate to a fair degree of accuracy the amount and depth of carburization. Fig. 15 is a photomicrograph of an as-hardened structure showing the usual austenitic grain boundaries, excess carbides, and grains common to the structure of hardened high speed steel. This photomicrograph shows that the edge is neither carburized nor decarburized. Figs. 16 to 21 inclusive show the
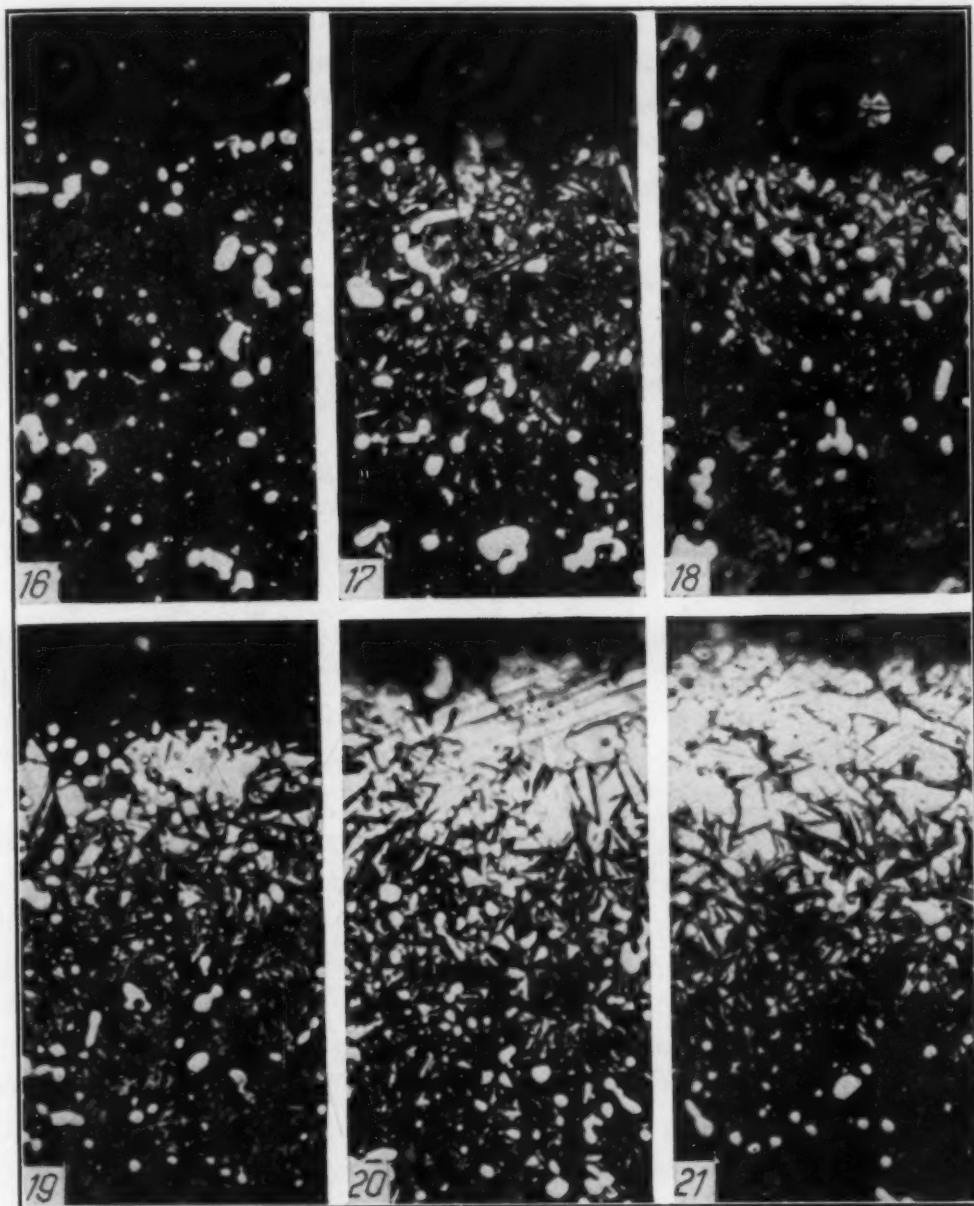
Figs. 16 to 21—The Relation of the Degree of Carburization to Microstructures All Oil-quenched 2350 Degrees Fahr., Drawn 1050 Degrees Fahr.—Surface Carbon of Machined Bar 0.72 Per Cent. Surface Carbon After Treating. × 1000.

Fig. 16—0.72 Per Cent.
Fig. 17—0.76 Per Cent.
Fig. 18—0.81 Per Cent.

Fig. 19—0.84 Per Cent.
Fig. 20—0.87 Per Cent.
Fig. 21—0.91 Per Cent.

structures of high speed steel as oil-quenched from 2350 degrees Fahr. (1290 degrees Cent.) and drawn at 1050 degrees Fahr. (565 degrees Cent.) for 1 hour. Fig. 16 shows neither carburization nor decarburization, while Fig. 21 shows a large amount of carburization. The four intermediate photomicrographs show different degrees of

carburization.   The carbon analysis on the machined bar before heat
treating was 0.72 per cent.   After heat treating, the carbon analysis
on the surface of the bars from which the photomicrographs were
taken were: Fig. 16—0.72 per cent; Fig. 17—0.76 per cent; Fig.
18—0.81 per cent; Fig. 19—0.84 per cent; Fig. 20—0.87 per cent;
Fig. 21—0.91 per cent.
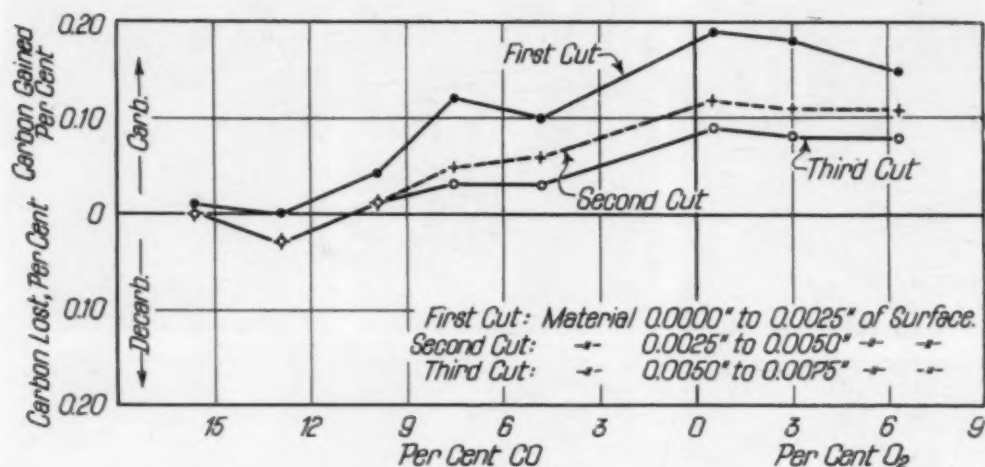
Fig. 22—Surface Carbon—Furnace Atmosphere Relationship As Affected by a 10-
Minute Soak in the Superheating Furnace. Specimens 1-Inch Round by 3 Inches Long.
Preheated 1550 Degrees Fahr.—2 Per Cent CO—Total Time 20 Minutes. Superheated
2350 Degrees Fahr.—Total Time 13 Minutes.
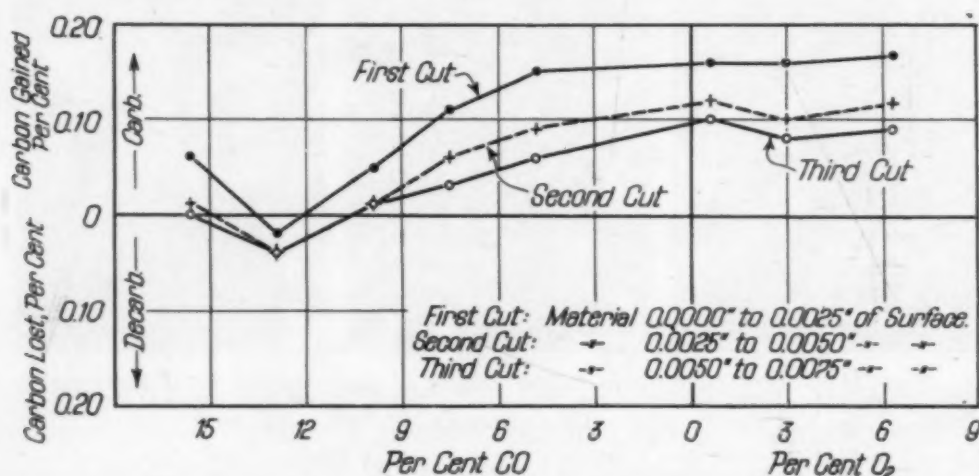
Fig. 23—Surface Carbon—Furnace Atmosphere Relationship as Affected by a 15-
Minute Soak in the Superheating Furnace. Specimens 1-Inch Round by 3 Inches Long.
Preheated 1550 Degrees Fahr.—2 Per Cent CO—Total Time 20 Minutes. Superheated
2350 Degrees Fahr.—Total Time 18 Minutes.

The structure caused by carburization is essentially a mixture
of retained austenite and some martensite.   The carbon concentration
in these areas is sufficiently high to prevent the austenite from com-

pletely transforming into martensite during the normal quench. The large black needles seen in the austenitic matrix are the result of a partial transformation of some of the austenite into martensite. A similar structure is commonly encountered when the quenching of high speed steel is interrupted (7) and the material tempered before it is sufficiently cold for complete hardening.

6. *The Effect of Variable Time and Variable Atmospheres with Constant Temperature*—The results as shown in Figs. 1 to 10 inclusive were obtained on tests which were treated from 2350 degrees Fahr. (1690 degrees Cent.) for normal treating times (i.e., for periods of 3.5 to 5 minutes total time) in the high heat furnace. To obtain some information on longer time in the superheat, two additional tests were run with atmospheres ranging from 15.5 per cent CO to 6.3 per cent O_2. Sections for these two tests were 1-inch round by 3 inches long, and were machined from bar stock $1\frac{1}{4}$-inch round. For both tests, the sections were preheated in an atmosphere of 2 per cent CO to a temperature of 1550 degrees Fahr. (845 degrees Cent.) for a total time of 20 minutes. Those for the first test were in the superheat furnace at 2350 degrees Fahr. (1290 degrees Cent.) for a total time of 13 minutes (approximately 10 minutes at heat); those of the second test were in the superheat furnace at the same temperature for a total time of 18 minutes (approximately 15 minutes at heat). The results are shown in Fig. 22 for the 10-minute soak, and Fig. 23 for the 15-minute soak. As will be observed from these curves, all tests showed carburization except those treated in the 12.8 per cent CO atmosphere. These two tests were practically neutral, showing neither carburization nor decarburization. Microscopic examination of the two samples confirmed that they were neither carburized nor decarburized. Again, it will be observed that those tests run in the oxidizing atmospheres had considerable carburization, and the carbon penetration in these particular tests was greater than in any of the previous tests.

7. *The Effect of Variable Time with Constant Atmosphere and a Constant Temperature*—The results under subdivision 6, (Part I), indicated that decarburization may take place in an atmosphere, which under normal treating conditions causes carburization, if the time in the superheat is prolonged. This was indicated in the tests which were held 10 to 15 minutes at heat in a 12.8 per cent CO atmosphere.

To establish whether an atmosphere which causes carburization in a short time will cause decarburization if the time is increased, test samples from ten different melts of steel were treated for various lengths of time in the superheat. The sections were ½ inch round by 1 inch long, and were machined from bar stock ⅝ inch round or larger. All sections were preheated to 1550 degrees Fahr. in a 2 per cent CO atmosphere for a total time of 15 minutes. The treating temperature was 2350 degrees Fahr. and the superheating atmosphere analyzed 6.8 per cent CO_2 and 10.2 per cent CO. The times at heat were 2.5, 5, 10, 15, 20, 30 and 40 minutes. Specimens were oil-quenched, followed by tempering at 1050 degrees Fahr. (565 degrees Cent.) for a total time of 1.5 hours. The size of the specimens did not permit chemical carbon analysis, but microscopic examination showed that all samples held at heat 10 minutes or less were carburized. Specimens held 15 minutes at heat were neutral or slightly decarburized. Six of the 15-minute samples were neutral and four showed traces of decarburization. Tests held 20 minutes or longer at heat showed decarburization, the amount of decarburization increasing with increase in time. These results definitely proved that an atmosphere which will cause carburization for short treating times will decarburize when the time is increased. The above data should be applied practically with some reservation, since it is possible that other temperatures, types of furnace, atmospheres, etc., will show different results.

8. *The Effect of Variable Time and Variable Temperature with a Constant Atmosphere*—Under subdivision 7, (Part I), it was established that atmospheres which carburize in a short time may cause decarburization if the time at heat is increased. For example, with a 10 per cent CO atmosphere and a temperature of 2350 degrees Fahr., the time at heat, before decarburization took place, was around 15 minutes.

As a result of these findings, it was deemed advisable to learn the effect of a constant atmosphere with variable times and different temperatures. To this end two separate tests were conducted. The first consisted of heating samples 0.5 inch square by 4 inches long from six different melts of steel in an atmosphere of 10 per cent CO to temperatures of 1900, 2000, 2100, 2200, 2300 and 2400 degrees Fahr. (1040, 1095, 1150, 1205, 1260 and 1315 degrees Cent.). The 0.5 inch squares were machined from bars ⅝ inch square or larger, and during the machining equal amounts were removed from all four
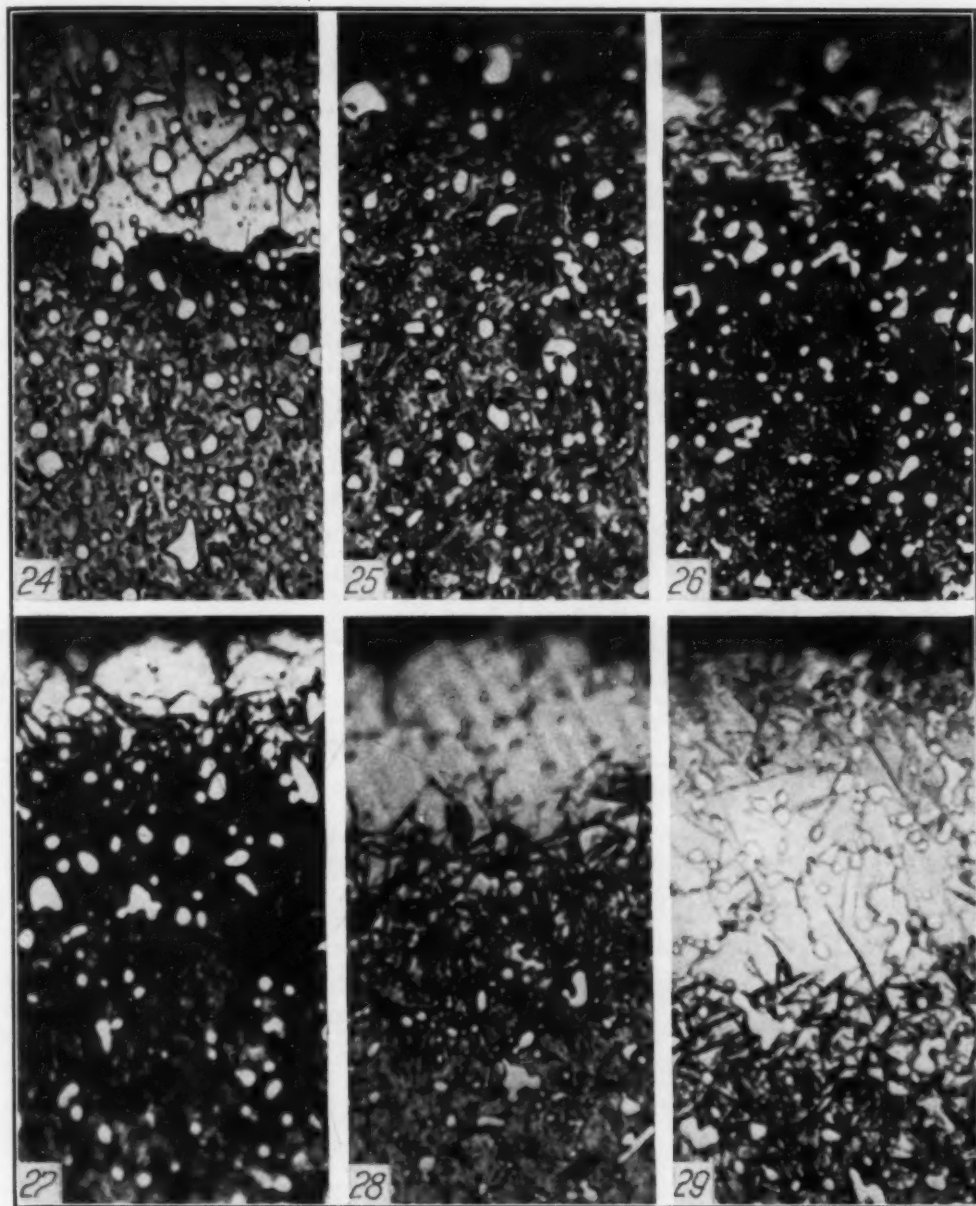
Figs. 24 to 29—The Effect of Constant Atmosphere with Variable Temperature Upon Microstructure (Edge). All Drawn 1050 Degrees Fahr. After Oil Quenching. × 1000. Fig. 24—Oil-Quenched 1900 Degrees Fahr. Fig. 25—Oil-Quenched 2000 Degrees Fahr. Fig. 26—Oil-Quenched 2100 Degrees Fahr. Fig. 27—Oil-Quenched 2200 Degrees Fahr. Fig. 28—Oil-Quenched 2300 Degrees Fahr. Fig. 29—Oil-Quenched 2400 Degrees Fahr.

sizes to eliminate surface condition. The preheating was done from a temperature of 1550 degrees Fahr. (845 degrees Cent.) in an atmosphere of 2 per cent CO for a total time of 20 minutes. The length of time in the superheat furnace ranged from 7 minutes for the 1900 degrees Fahr. treatment to 2.5 minutes for the 2400 degrees

Fahr. treatment; proportionate times for the other superheating temperatures. After oil quenching, sections were drawn at 1050 degrees Fahr., 1 hour at heat. Fig. 24 shows the microstructure of a specimen treated from 1900 degrees Fahr. (1040 degrees Cent.) and shows decided decarburization; Fig. 25, the structure of a sample treated from 2000 degrees Fahr. (1095 degrees Cent.), showing

Table II
The Effect of Time and Temperature with Constant Atmosphere on Surface Carbon

Oil Treating Temp. Degrees Fahr.	2 Min. at Heat Cut 1	Cut 2	Cut 3	6 Min. at Heat Cut 1	Cut 2	Cut 3	10 Min. at Heat Cut 1	Cut 2	Cut 3	15 Min. at Heat Cut 1	Cut 2	Cut 3
2000	0.74	0.71	0.72	0.70	0.66	0.67	0.64	0.63	0.65	0.57	0.59	0.62
2100	0.83	0.75	0.73	0.79	0.71	0.73	0.72	0.70	0.70	0.70	0.67	0.68
2200	0.97	0.85	0.77	0.85	0.77	0.74	0.83	0.75	0.74	0.79	0.74	0.72
2250	0.95	0.80	0.76	0.89	0.77	0.75	0.83	0.74	0.74	0.75	0.72	0.72
2300	0.94	0.80	0.76	0.91	0.79	0.76	0.83	0.74	0.74	0.83	0.75	0.74
2350	0.93	0.79	0.77	0.91	0.79	0.75	0.87	0.77	0.74	0.84	0.74	0.70
2400	0.89	0.77	0.76	0.88	0.71	0.69	0.80	0.72	0.69	0.72	0.66	0.65
2450	0.96	0.81	0.76	0.92	0.77	0.73	0.78	0.75	0.70	0.50	0.46	0.49

Specimens 1 inch round by 3 inches long—Preheated 1550 degrees Fahr.—2 per cent CO atmosphere—total time 20 min.
Superheated to temperatures indicated in an atmosphere of 9.8-11.0 per cent CO.
Carbon analysis of machined bar prior to treating 0.71-0.72 per cent.
Cut 1 = 0.0000-0.0025 inch. Cut 2 = 0.0025-0.0050 inch. Cut 3 = 0.0050-0.0075 inch.

neither carburization nor decarburization; Figs. 26 to 29 inclusive—the structures of samples treated from 2100 to 2400 degrees Fahr. (1150 to 1315 degrees Cent.) respectively. It will be noted that from 2100 to 2400 degrees Fahr. carburization took place and the higher the treating temperature the greater the degree of carburization. These findings were checked by treating test sections 1-inch round by 3 inches long from temperatures of 2000 to 2450 degrees Fahr. (1095 to 1345 degrees Cent.) in increments of 50 degrees Fahr. except between 2000 and 2200 degrees Fahr. (1205 degrees Cent.), where the increment was 100 degrees Fahr. Tests were preheated in the usual manner, i.e., 1550 degrees Fahr. (845 degrees Cent.)—20 minutes—2 per cent CO atmosphere. The times at heat in the high temperature furnace were 2, 6, 10 and 15 minutes. The atmosphere in the superheat furnace varied between 9.8 and 11 per cent CO for the times mentioned above. After oil quenching, samples for chemical analysis were prepared in the usual manner.

Results of the chemical carbon analysis are given in Table II, and those of the first cut (0.0000 to 0.0025 inch) are plotted in Fig. 30. The carbon analysis of the bar in the machined condition was

0.71 to 0.72 per cent. When treating from 2000 degrees Fahr. (1095 degrees Cent.) the carbon analysis for the sample held 2 minutes at heat was practically neutral showing a slight tendency toward carburization. The sections treated from 2000 degrees Fahr. (1095 degrees Cent.), held 6 minutes at heat, showed slight decarburization; those treated from 2000 degrees Fahr. (1095 degrees Cent.), held 10 and 15 minutes at heat showed definite decarburization. Those

Table III
The Effect of Atmospheres of 16 Per Cent CO or Higher

Atmosphere			Total Time in Superheat 10 Min.			Total Time in Superheat 20 Min.		
			Cut 1	Cut 2	Cut 3	Cut 1	Cut 2	Cut 3
CO_2	O_2	CO	0.0000-0.0025"	0.0025-0.0050"	0.0050-0.0075"	0.0000-0.0025"	0.0025-0.0050"	0.0050-0.0075"
6.4	0.0	13.3	0.80	0.76	0.75	0.76	0.71	0.70
4.0	0.0	16.4	0.46	0.48	0.55	0.48	0.46	0.47
3.6	0.0	19.4	0.46	0.47	0.57	0.54	0.55	0.60
2.8	0.0	24.4	0.75	0.71	0.70	0.80	0.72	0.70
2.0	0.0	27.0	0.70	0.64	0.65	0.70	0.65	0.65

Specimens 1 inch round by 3 inches long—No preheat.
Superheated to 2350 degrees Fahr. for total times indicated above.
Carbon analysis on machined bar prior to treating 0.70-0.71 per cent.

treated from 2100 degrees Fahr. (1150 degrees Cent.) showed slight carburization when held 2 or 6 minutes at heat, while the one treated from the same temperature and held 10 minutes at heat was neutral, and finally the one held 15 minutes at heat at 2100 degrees Fahr. (1150 degrees Cent.) showed a tendency toward decarburization. All tests treated from temperatures of 2200 to 2350 degrees Fahr. were carburized, even up to 15 minutes at heat. However, it is interesting to note that the greatest carburization was found with the shortest holding time in each case, and the amount of carburization decreased as the holding time increased. When treating from 2400 degrees Fahr. (1315 degrees Cent.) the first three samples showed carburization, while the one held 15 minutes at this temperature showed slight decarburization. Again, the degree of carburization decreased with increase in time at heat. The first three sections treated from 2450 degrees Fahr. (1345 degrees Cent.) were carburized, while the one held 15 minutes at this temperature showed definite decarburization. These results show that both time and temperature have a definite influence on the amount of carburization.

9. *The Effect of Atmospheres Containing 16 Per Cent CO or Higher*—Throughout this study, atmospheres of 16 to 16.5 per cent

CO gave inconsistent results. When the atmospheres varied between 15.5 and 16.0 per cent CO for normal treating times, carburization was usually found; atmospheres containing 16 per cent CO or higher frequently caused decarburization.

A more thorough check of this effect was studied by using atmospheres of 13.3 to 27.0 per cent CO. The usual size specimen, 1 inch round by 3 inches long, was used. The limit of CO in the controlled atmosphere electric furnace was around 16 per cent CO, consequently a separate generator was employed to develop the higher
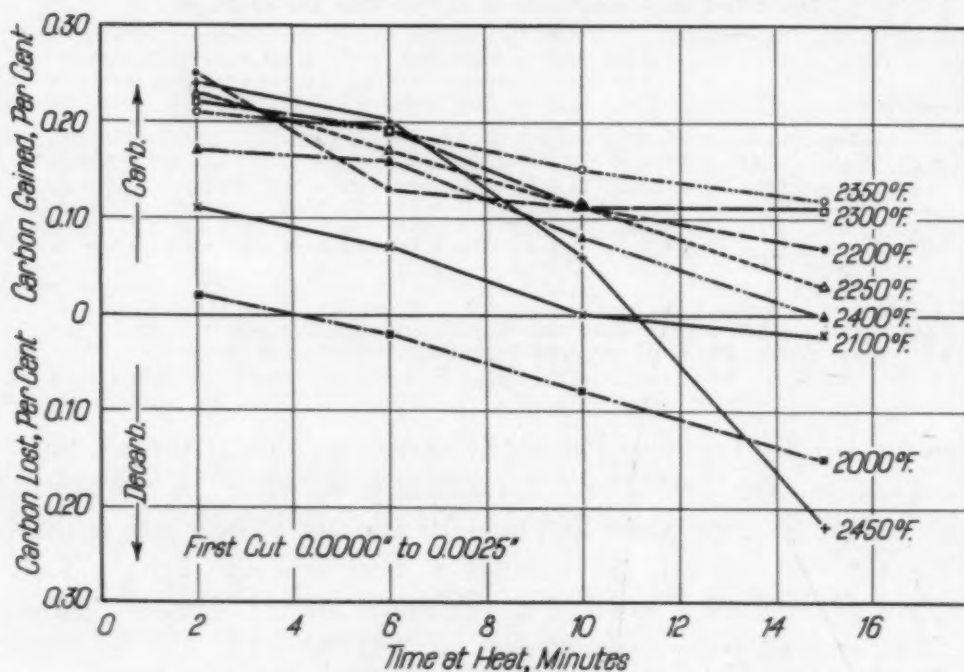
Fig. 30—Surface Carbon—Furnace Atmosphere Relationship as Affected by Variable Time—Variable Temperature—With a Constant Atmosphere. Specimens 1-Inch Round by 3 Inches Long—Preheated 1550 Degrees Fahr.—2 Per Cent CO—Total Time 20 Minutes. Superheated to Temperatures and for Times Indicated in a 10.0 to 11.0 Per Cent CO Atmosphere.

CO atmospheres. This generator consisted of a wrought iron pipe, 18 inches in diameter by 30 inches long, the ends of which were welded with suitable caps. A convenient inlet and outlet were arranged for passing air into the generator, and for delivery of the CO to the superheating furnace. The entire generator was filled with wood charcoal, and the complete unit was heated to 1830 degrees Fahr. (1000 degrees Cent.). The CO was generated by passing air over the hot charcoal, the air being preheated prior to entering the generator proper. Atmospheres of 13.3 and 16.4 per cent CO were secured without the use of the previously mentioned generator.

The other three atmospheres were obtained by diluting the furnace
atmospheres with generated CO. None of the samples were pre-
heated since the preheating furnace had to be used to operate the gas
generator. Two tests were run at a temperature of 2350 degrees
Fahr. (1290 degrees Cent.), the first for a total time of 10 minutes,
the second for a total time of 20 minutes. The results of these tests
are given in Table III.

These results show that samples treated in a 13.3 per cent CO
atmosphere were carburized; while those treated in a 16.4 and 19.4
per cent CO atmosphere were definitely decarburized.
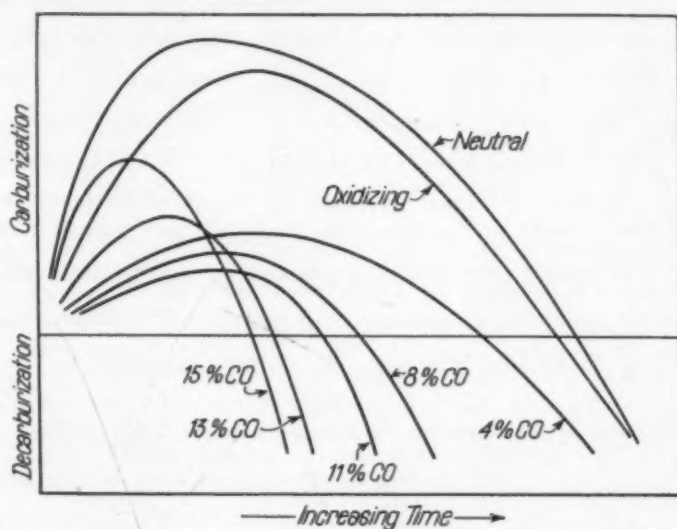
Fig. 31—Probable Curves Showing the Relationship of
Time and Atmosphere to Surface Carbon When Treated from
a Temperature of 2350 Degrees Fahr. These Curves Have
Not Been Derived, but are Based Upon Data Obtained to
Date.

When the percentage of CO was around 24.0 to 27.0 per cent
CO, the surface carbon was practically neutral. Undoubtedly an
atmosphere containing 32.0 per cent CO would cause carburization,
as has been established by atmospheres generated with carbon blocks.

10. *Probable Curves for Time, Atmosphere and Temperature
Relationship*—Reviewing the results of all the foregoing tests, there
is definite evidence of changes which take place on the surface of
18-4-1 high speed steel with variations in atmosphere, time and
temperature. Figs. 1 to 10 inclusive, which represent normal treating
times from several types of furnaces, employing different gases for
controlling the furnace atmospheres, show clearly that carburization
takes place when treating from 2350 degrees Fahr. The only excep-

tions were the two tests treated by one of the co-operative firms in high CO atmospheres.

Under subdivision 6 (Part I), the length of time at heat was studied and the general tendency was first to carburize, and as the time increased, the amount of carburization decreased. Under subdivision 7 (Part I), time and temperature were found to have a definite influence on both carburization and decarburization. On the

Table IV
The Effect of Long Soaking Time on Surface Carbon

	Atmosphere		Cut 1	Cut 2	Cut 3	Cut 4
CO_2	O_2	CO	0.0000-0.0025″	0.0025-0.0050″	0.0050-0.0075″	0.0075-0.0100″
5.4	0.0	14.5	0.62	0.64	0.61	0.62
6.4	0.0	12.1	0.58	0.59	0.57	0.59
8.6	0.0	7.7	0.57	0.64	0.64	0.65
10.2	0.0	5.0	0.59	0.72	0.71	0.71
12.6	0.6	0.0	0.77	0.78	0.77	0.71
10.1	4.6	0.0	0.76	0.80	0.79	0.77
7.4	9.3	0.0	0.75	0.79	0.79	0.78

Specimens 1.5 inch round by 3 inches long—Preheated 1550 degrees Fahr.—2 per cent CO—Total time 40 minutes.
Superheated 2350 degrees Fahr.—0.5 hour—atmospheres indicated above.
Carbon analysis on the machine bar 0.71-0.72 per cent.

Table V
Effects of Atmospheres on Elements Other Than Carbon

	Atmosphere		Cut 1	Cut 2	Cut 3	Silicon	Chromium	Tungsten	Vanadium
CO_2	O_2	CO							
As machined			0.75	....	....	0.24	3.84	18.42	1.07
4.7	0.0	15.3	0.82	0.74	0.74	0.24	3.85	18.40	1.09
5.9	0.0	12.4	0.87	0.75	0.74	0.22	3.85	18.55	1.11
7.2	0.0	10.0	0.81	0.77	0.74	0.25	3.85	18.52	1.11
9.8	0.0	5.5	0.87	0.78	0.75	0.23	3.84	18.50	1.11
13.0	0.0	0.6	0.85	0.77	0.76	0.24	3.85	18.46	1.09

Specimens 1⅞ inches round by 5 inches long—Preheated 1550 degrees Fahr.—2 per cent CO—Total time 40 minutes.
Superheated 2350 degrees Fahr.—5 minutes at heat.
Analysis of elements other than carbon made on material from the first cut (0.0000-0.0025 inch).

basis of the foregoing information, the author has ventured to predict the type and shape of curves which can be expected with variations in time and furnace atmosphere at 2350 degrees Fahr. These probable curves are shown in Fig. 31. It is imperative to stress that these curves have not been derived from a complete series of tests for each of the indicated atmospheres, but are based upon results of the different tests conducted to date. For instance, the curves in Fig. 30 show the behavior of one atmosphere for relatively short

times.   The results obtained on 1.5-inch rounds treated from 2350 degrees Fahr. (1290 degrees Cent.), using seven different atmospheres, gave additional evidence that these probable curves represent a condition which may be expected.   These sections were held at heat 30 minutes, oil-quenched, annealed in lead, and surface carbon analyses determined.   These data are shown in Table IV.   The four sections treated in a reducing atmosphere showed decarburization, while the three sections treated in the oxidizing atmospheres were carburized.   Considerable time would be required to fully establish these curves and the cost undoubtedly would be prohibitive.   Such factors as time at heat, temperature, gas analysis, and type of fuel for developing the furnace atmospheres would have to be given due consideration.   A rough calculation shows the number of carbon analyses necessary to definitely establish the shape of these curves to be approximately 6000.   In addition to carbon analysis, microscopic examination should be used to confirm results.   It is obvious that a test of this nature could be extended.

11.   *The Effect of Atmospheres on Elements Other Than Carbon*—The chemistry to this point in the investigation was confined to carbon.   The other elements of interest in 18-4-1 high speed steel are chromium, tungsten and vanadium.   In view of the carbon behavior, it is logical to ask: "What effect does atmosphere have on these other elements?"   This problem was studied as follows:

Sections 2 inches round by 5 inches long were machined to 1⅞-inch round.   The preheating was done at a temperature of 1550 degrees Fahr. (845 degrees Cent.) in a 2 per cent CO atmosphere for a total time of 40 minutes.   The superheating temperature was 2350 degrees Fahr. (1290 degrees Cent.) and the sections were held at heat 5 minutes.   The atmospheres ranged from 15.3 CO to 0.6 per cent CO.   The data for these tests are given in Table V which shows that the other elements are unaffected by furnace atmosphere.   The analyses given in Table V for elements other than carbon were taken from turnings representing the first cut of 0.005 inch on the diameter.   Attention is called to the fact that these relatively large sections showed carburization throughout the range of atmospheres tested.

12.   *The Effect of Drawing (Tempering) on Carburized Areas*—The carburization which takes place during normal heat treating as previously mentioned cannot be seen in the as-hardened condition.   Drawing at temperatures of 950 to 1100 degrees Fahr. (510 to 595 degrees Cent.) for periods of 1 hour or less reveals the carburized

zone either as dark acicular martensitic needles or frequently as a white band of austenite, in which the dark needles appear. If the amount of austenite is relatively large, the austenitic areas near the edge will be free from large martensitic needles, but if an examination is made from the edge of the sample toward the uncarburized material, it will be found that these needles will eventually appear; invariably lying between the uncarburized material and the highly carburized zone.

It was believed that the carburization which takes place in normal heat treating would show the same characteristics as a section purposely carburized. To study the behavior of a carburized area more carefully and to have larger fields for investigation, a sample 1-inch round by 3 inches long was preheated to a temperature of 1600 degrees Fahr. in a wood charcoal pack for a total time of 6.5 hours (approximately 5 hours at temperature). Following the carburizing preheat, the section was removed from the pack, and transfered to the high speed furnace, which was running at 2350 degrees Fahr. (1290 degrees Cent.). The highly carburized surface was protected during the high heat treatment with a carbon block, and was held in the carbon block at the temperature mentioned for 10 minutes, followed by oil quenching. Fig. 32 shows the structure of this carburized area in the as-hardened condition. The structure is identical with any normally treated 18-4-1 high speed steel except for the small amount of eutectic shown on the surface. The structure consists of the usual grain boundaries and excess carbides. The same microspecimen was drawn at 1050 degrees Fahr. (565 degrees Cent.) for 1 hour, and the structure after this treatment is shown in Fig. 33. This photomicrograph shows that the eutectic was unaffected by tempering; directly back of the eutectic there is a field of austenite, and adjoining the austenitic field, the structure is composed of dark acicular martensitic needles in retained austenite. The structure of these dark needles is better shown in Fig. 34 which was taken 0.0035 inch from the edge of the same microspecimen from which Fig. 33 was taken. The entire field is composed of dark needles in an austenitic matrix. This type of structure is frequently encountered when the quenching of high speed steel is interrupted. It must be stressed that the quench of this particular specimen was not interrupted since it was lying around in the as-hardened condition for two days before any microscopic examination was made. The structures shown in Figs. 33 and 34 clearly indicate that the retained
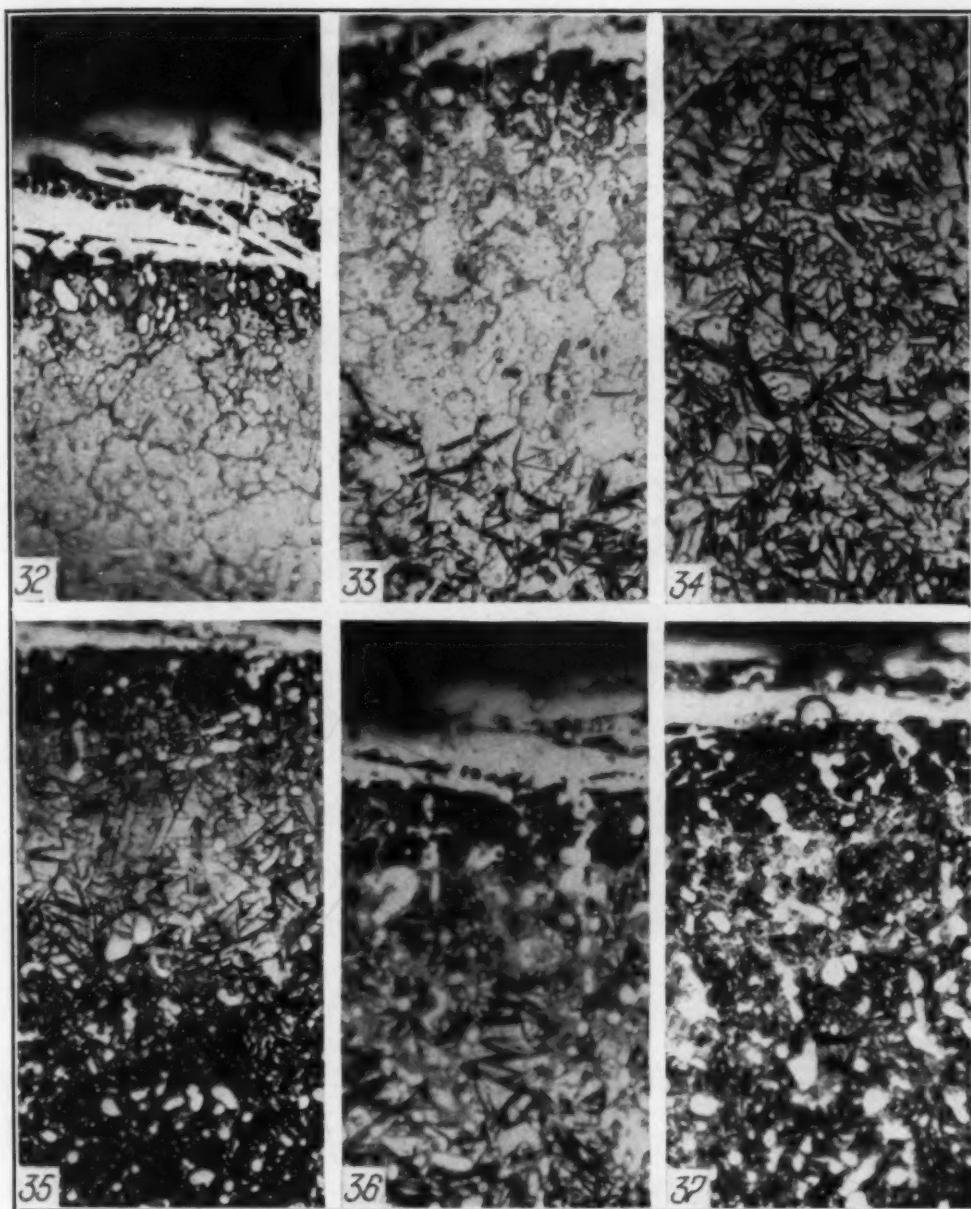
Figs. 32 to 37—The Effect of Repeated Tempering Upon Microstructure of Material Carburized in Wood Charcoal. × 750. Fig. 32—Preheated in Charcoal Pack 1600 Degrees Fahr., 6½ Hours, Oil-quenched 2350 Degrees Fahr. Fig. 33—Same as Fig. 32 After Tempering 1050 Degrees Fahr. for One Hour. Fig. 34—Same as Fig. 33—Taken 0.0035 Inch from Edge of Specimen. Fig. 35—Same as Fig. 33—After a Second Drawn for 2 Hours at 1050 Degrees Fahr. Fig. 36—Same as Fig. 33—After a Third Draw for 2 Hours at 1050 Degrees Fahr. Fig. 37—Same as Fig. 33—After a Fourth Draw for 16 Hours at 1050 Degrees Fahr.

austenite has partially broken down. Incidentally the structure of the specimen which was not carburized showed the usual drawn structure for this type of steel. The same microspecimen was given a second draw from a temperature of 1050 degrees Fahr. (565 de-

grees Cent.), 2 hours at heat, total time 2.5 hours. The structure
after the second tempering operation, as shown in Fig. 35 indicates
that the retained austenite transformed still further to martensite.
The area which had been practically all austenite after the first draw
has broken down and is composed of dark martensitic needles in the
austenite. The area directly in back of this austenitic band which
showed martensitic needles in austenite on the first draw (see Fig.
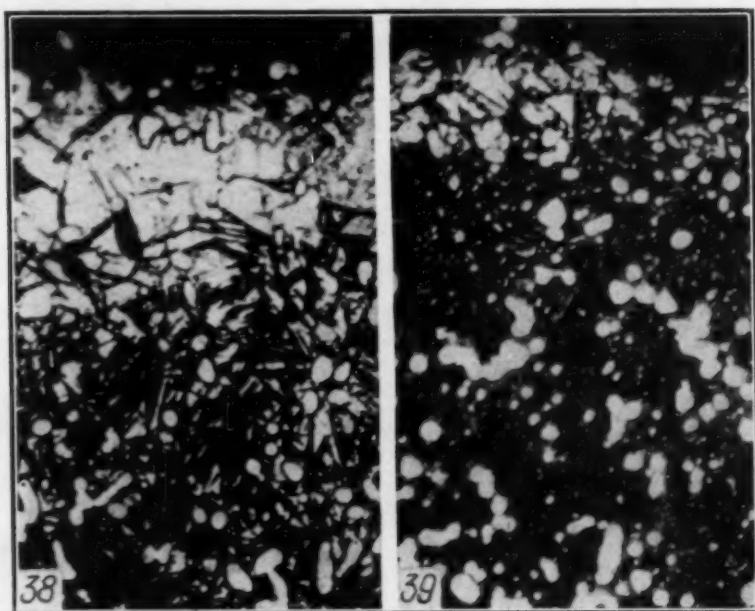
Figs. 38 and 39—The Effect of Long Time Re-tempering upon
the Microstructure of Carburized Material. Carburization Took
Place During Normal Treating. X 1000. Fig. 38—Oil-quenched
2350 Degrees Fahr., Drawn at 1050 Degrees Fahr.—Surface Carbon
as Machined 0.74 Per Cent; As Treated 0.89 Per Cent. Fig. 39—
Taken from the Same Microspecimen as Fig. 38 After Re-tempering
at 1050 Degrees Fahr. for 12 Hours.

34) was composed of a mass of black needles after the second draw.
The microspecimen was given a third draw at 1050 degrees Fahr.
(565 degrees Cent.), 2 hours at heat, total time 2.5 hours. The
structure after the third drawing operation, as shown in Fig. 36,
indicates that the retained austenite has broken down still further.
Finally the microspecimen was given a fourth draw at 1050 degrees
Fahr. for a total time of 16 hours. The structure clearly indicates
that all of the retained austenite has broken down into martensite,
as shown in Fig. 37.

To correlate these various microstructures with the carbon con-
tent, surface carbon analyses were made on the 1-inch round bar
from which the above microspecimen was taken. The results of these

analyses on steps of 0.005 inch on the diameter are shown as follows:

Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8
1.05%	0.98%	0.98%	0.99%	0.99%	0.99%	0.97%	0.95%

The microscopic examination after the first drawing treatment showed that the eutectic averaged between 0.0007 and 0.0010 inch; the retained austenite averaged between 0.0020 and 0.0025 inch; and finally a mixture of retained and transformed austenite which is characterized by the black martensitic needles 0.025-0.030 inch. The in-
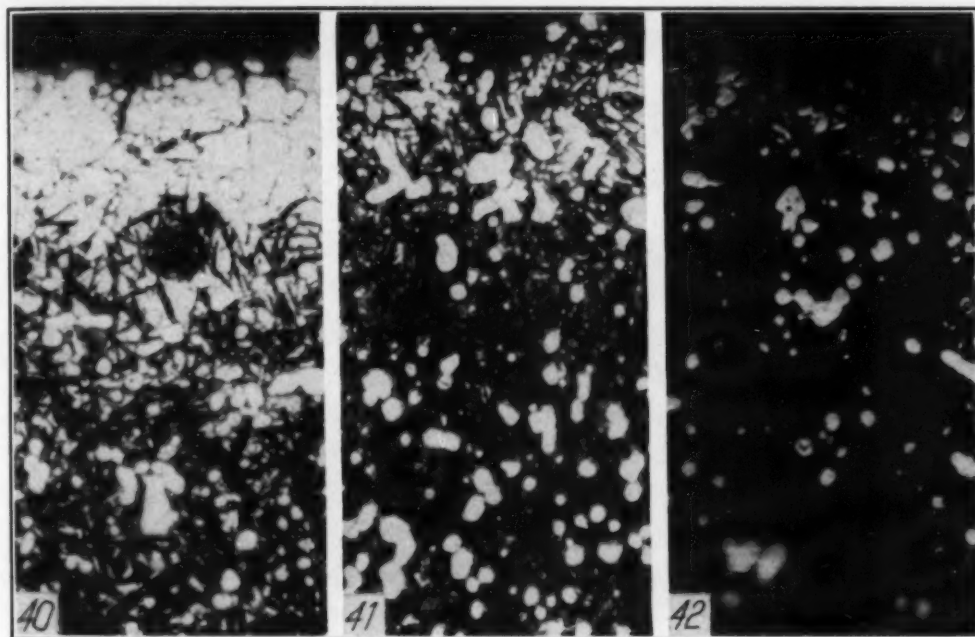
Figs. 40 to 42—The Effect of Triple Tempering Upon Carburized Material. Carburization Took Place During Normal Treating. × 1000. Fig. 40—Oil-quenched 2350 Degrees Fahr., Drawn 1050 Degrees Fahr. Surface Carbon on Machined Bar 0.74 Per Cent; As Treated 0.92 Per Cent. Fig. 41—Same as Fig. 40 After a Second Draw at 1050 Degrees Fahr. for 2 Hours. Fig. 42—Same as Fig. 40 After a Third Draw at 1050 Degrees Fahr. for 2 Hours.

dications from these results are that in order to have retained austenite, the carbon content must be between 0.95 and 1.05 per cent. Partially transformed austenite as shown in Fig. 34 requires 0.90-0.98 per cent carbon. The amount and nature of the black needles depends entirely upon the carbon concentration. When only a few needles appear the carbon concentration is high; while when the entire structure shows a mass of black needles, the amount of carburization is small. A more detailed study of the relation between carbon content and microstructures will require further attention. If specimens of sufficient size, to insure enough sample for chemical

carbon analysis, can be heat treated without too great an amount of warpage, and if cuts of 0.0005 inch on the diameter can be obtained, a closer correlation between microstructure and carbon content will be established.

The foregoing study of a carburized section showed that the retained austenite due to high carbon concentration can be broken down on repeated drawing (8). Further confirmation of this observation was obtained on a section 0.5 inch square by 4 inches long which was preheated to a temperature of 1600 degrees Fahr. (870 degrees Cent.) in a wood charcoal pack for a total time of 11 hours. After preheating, the section was oil-quenched from 2350 degrees Fahr. (1290 degrees Cent.), and 0.002 inch ground from the surface to remove the eutectic constituent. The Rockwell hardness as oil-quenched was C-42-44; after drawing for a total time of 1.5 hours, at 1050 degrees Fahr., the Rockwell hardness was C-64-66. The Rockwell hardness after a second draw at 1060 degrees Fahr. (570 degrees Cent.) for 2 hours was C-69-70. The same section was given a third draw at 1090 degrees Fahr. (590 degrees Cent.) for 2 hours, after which it showed a Rockwell hardness of C-68-69. These hardness results confirm the presence of retained austenite caused by high carbon concentration and its decomposition during tempering.

Returning to specimens which were carburized during normal treating from 2350 degrees Fahr. (1290 degrees Cent.) a microspecimen was taken from a test which on chemical carbon analysis showed an increase in surface carbon of 15 points. Fig. 38 shows the structure as oil-quenched and drawn at 1050 degrees Fahr. for 1 hour. The structure shows a great deal of retained austenite and some dark acicular martensitic needles. The same microspecimen was redrawn at 1050 degrees Fahr. for a total time of 12 hours. The structure after this retempering operation is shown in Fig. 39, and by comparing the two structures, it is readily seen that a large percentage of the retained austenite broke down.

A second sample which showed an increase in surface carbon of 18 points was studied and Fig. 40 shows the structure of the edge after oil quenching from 2350 degrees Fahr. (1290 degrees Cent.) and tempering at 1050 degrees Fahr. (565 degrees Cent.) for 1 hour. Fig. 41 shows the edge after retempering for a 2-hour period at 1050 degrees Fahr. Fig. 42 shows the structure of the same sample after a third tempering operation for 2 hours at 1050 degrees Fahr. Fig. 42 shows a small amount of untransformed austenite. Examination

of this specimen after the third drawing operation showed that there
were only two or three small areas which had retained austenite, the
area as shown in Fig. 42 being the largest. Practically 95 per cent
of the retained austenite as shown in Fig. 40 transformed during
the second and third tempering operations.

On numerous occasions it has been reported that double drawing
increases the tool life. The behavior of the retained austenite during
tempering, which was caused by carburization, may be a partial
answer to this observation. It has just been shown that the rate at
which the retained austenite decomposes depends upon the carbon
concentration. When the amount of carburization is small, a double
draw at 1050 degrees Fahr. (565 degrees Cent.) is sufficient to break
down the retained austenite. However, when the carburization is
relatively high, as shown in the above two instances, the time or
the number of drawing operations must be increased to cause the
retained austenite to break down. It might be well to mention when
making microscopic examination of material that has been carburized
during heat treating, the carburized constituent will etch faster than
the uncarburized material. It is possible by carefully noting the
edge of the microspecimens to tell with the unaided eye whether or
not it is carburized due to the difference in shading. Further study
of the behavior of this retained austenite as affected by tempering is
warranted.

13. *The Effect of Atmospheres on Size and Weight Change*—
An important consideration in hardening is the surface condition of
the finished tools, as regard scaling, pitting, blistering, etc. The
surfaces of specimens after treating from the various atmospheres
and temperatures previously mentioned were carefully inspected. All
test sections regardless of the type of furnace or composition of at-
mosphere showed some scale. Those treated from 19.0-27.0 per cent
CO, considered highly protective, showed some scaling. In general
it was found that the higher the CO content of the furnace atmos-
phere, the smaller the amount of scale. In the atmosphere range of
13.0 to 15.0 per cent CO the amount of scale was relatively small.
In the range of 8.0 to 12.0 per cent CO the amount of scale adhering
to the surface was negligible, but a great portion of the scale formed
in this range was thrown in the quench. As the CO decreased below
8 per cent, the amount of scale remained fairly constant, showing a
tendency to increase with a decrease in the CO content. The amount
of scale in the oxidizing range was definitely greater than that of the

reducing atmospheres. The surface obtained in oxidizing atmospheres, in the author's opinion, are definitely unsatisfactory for the treating of the majority of tools made from this type of steel. In addition to a large amount of scale, oxidizing atmospheres always produce a rough surface, frequently causing pitting, and often show the condition commonly referred to as "alligator skin". Oxidizing

Table VI
The Effect of Atmospheres on Size and Weight Change

			As-Hardened 2350° F. Total Time 5 Min.			As-Hardened 2350° F. Total Time 10 Min.		
Atmosphere			Length Change Inch	Diameter Change Inch	Weight Loss Gram	Length Change Inch	Diameter Change Inch	Weight Loss Gram
CO_2	O_2	CO						
3.7	0.0	16.3	+0.0009	+0.0004	0.132	+0.0016	+0.0006	0.078
4.8	0.0	14.3	+0.0009	+0.0006	0.154	+0.0015	+0.0006	0.207
6.9	0.0	11.1	−0.0002	−0.0008	0.564	+0.0006	−0.0011	0.883
9.3	0.0	5.7	−0.0007	−0.0015	0.737	−0.0015	−0.0036	1.428
11.2	0.0	3.5	−0.0013	−0.0019	0.912	−0.0031	−0.0038	1.895
12.0	0.9	0.0	−0.0016	−0.0032	1.200	−0.0048	−0.0068	2.832
9.3	4.1	0.0	−0.0020	−0.0040	1.581	−0.0060	−0.0081	3.439
			As-Hardened 2350° F. Drawn 1050° F. Total Time in Superheat 5 Min.			As-Hardened 2350° F. Drawn 1050° F. Total Time in Superheat 10 Min.		
3.7	0.0	16.3	+0.0011	+0.0004	0.229	+0.0021	+0.0010	0.154
4.8	0.0	14.3	+0.0011	+0.0007	0.203	+0.0017	+0.0004	0.264
6.9	0.0	11.1	+0.0002	−0.0006	0.712	−0.0008	−0.0010	0.998
9.3	0.0	5.7	−0.0006	−0.0011	0.845	−0.0018	−0.0030	1.550
11.2	0.0	3.5	−0.0010	−0.0019	1.032	−0.0031	−0.0040	1.952
12.0	0.9	0.0	−0.0012	−0.0025	1.278	−0.0062	−0.0068	2.884
9.3	4.1	0.0	−0.0016	−0.0032	1.715	−0.0065	−0.0082	3.597

Specimens 1-inch round by 1-inch long—Preheated 1550 degrees Fahr.—2 per cent CO —20 min.
Size change determined with a four-place micrometer.
Weight change determined with standard analytical balance.
After all heat treating operations samples mechanically cleaned by sand blasting.

atmospheres further caused sharp corners or edges to become round due to scaling.

These general observations of the effect of atmospheres on surface were checked by making both weight and size change determinations. Test sections 1-inch round by 1-inch long were heated to a temperature of 2350 degrees Fahr., in atmospheres ranging from 16.0 per cent CO to 4.0 per cent O_2. It was necessary to use this relatively small size in order not to exceed the sensitivity of the analytical balance. The samples were carefully cleaned in petroleum ether prior to weighing. All samples were preheated in a 2 per cent CO atmosphere to a temperature of 1550 degrees Fahr. for a total time of 20 minutes. Two separate tests were made; in the first, samples were held in the superheat for a total time of 5 minutes; in the second, the time in the high temperature furnace was 10 minutes.

Two samples were treated under each of the above conditions; one was examined in the as-hardened condition; the second, after drawing at 1050 degrees Fahr. for a total time of 1.5 hours. Following all heat treating operations, the samples were mechanically cleaned by sand blasting. They were allowed to remain in the sand blast only long enough to remove the scale. Results of this test are given in
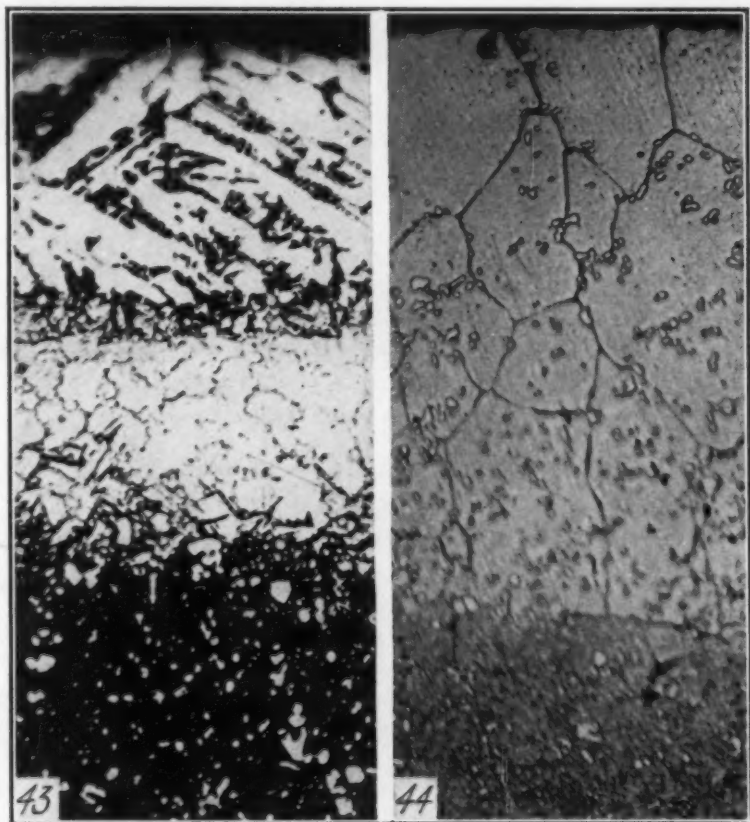
Fig. 43—Oil-quenched 2350 Degrees Fahr., Drawn 1050 Degrees Fahr. Carburized Zone at Base of a Blind Hole. × 500.
Fig. 44—Oil-quenched 2350 Degrees Fahr., Drawn 1050 Degrees Fahr. Decarburization Caused by Surface Contact of the Material with the Furnace Hearth. × 500.

Table VI. A study of these data shows several interesting effects:

1. As the CO content of the furnace atmosphere decreases, or the O_2 increases, the weight loss increases.

2. When the scalage is low, changes in structural composition compensate for the loss in size due to scalage.

3. The weight loss after drawing in a still air electric furnace at 1050 degrees Fahr. for a total time of 1.5 hours is slightly greater than in the as-hardened condition.

4. Loss in size (or volume) increases as the CO decreases or the O_2 increases.

5. Increasing the time in any atmosphere increases the amount of scalage as indicated by weight loss.

It is realized that the surface area-volume ratio will have a definite bearing on the amount of scale as determined by weight loss. However, this test served admirably to determine the effect of furnace atmospheres on scalage. This test indicates that the higher the CO, the better the surface condition after treating. This is true if
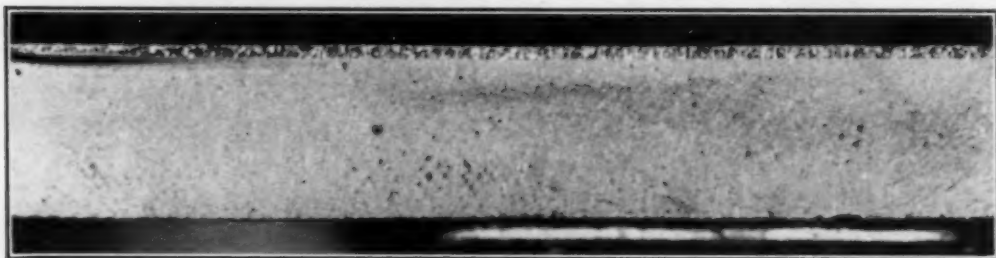
Fig. 45—Decarburization Caused on Surface in Contact with Hearth When Oil-quenched from 2350 Degrees Fahr. Decarburization in this Type of Steel is Generally Characterized by Very Coarse Grains. $\times$ 2.

surface appearance is the only consideration, but as previously shown, when the CO content is around 16 per cent, decarburization usually takes place.

14. *Miscellaneous Tests*—The foregoing information indicates that the heat treatment of 18-4-1 high speed steel is a rather simple operation; however, there are certain exceptions to the general rules, of which the following are examples:

Sections which have blind holes present a problem. A study of several sections which had blind holes invariably showed some areas to be decarburized while other areas showed carburization. A more thorough study of sections of this type was made as follows: Six specimens 1 inch round by 3 inches long with a 0.5 inch hole, drilled longitudinally 2.5 inches deep, were treated in atmospheres of 15.5, 9.8 and 4.8 per cent CO; 0.5, 3.0 and 6.3 per cent O_2. These samples were preheated in a 2 per cent CO atmosphere at 1550 degrees Fahr. for 15 minutes, followed by superheating to 2350 degrees Fahr. for a total time of 5 minutes. The examination of these specimens regardless of the furnace atmosphere showed that the entrances to the holes were badly decarburized, while the bottoms were excessively carburized; in fact, they carburized to such an extent that some eutectic was present. Fig. 43 shows the microstructure of the base of one

of these holes. An examination of this photomicrograph shows that the carburized area has four distinct fields; first—eutectic; second—untransformed austenite; third—partially transformed austenite (which is characterized by the martensitic needles); fourth—a normal structure. Several tests were made with slightly smaller and slightly
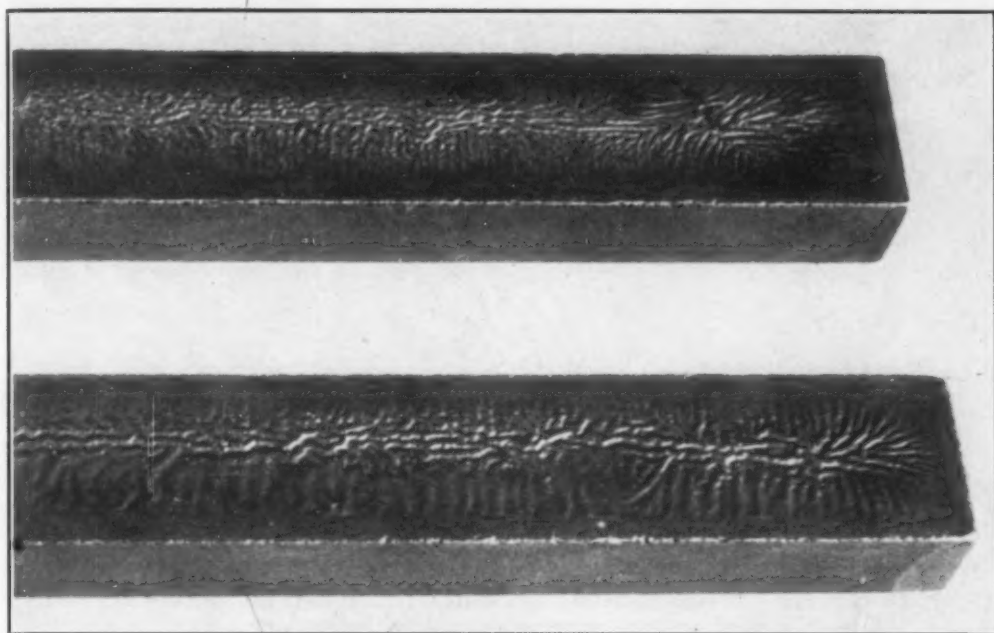
Fig. 46—Wrinkled Surfaces Caused by Excessive Carburization. This Condition May Occur on Contact Surface in Highly Reducing Atmospheres. Actual Size.

larger than 0.5 inch holes. In each instance it was found that both decarburization and carburization took place. Examination of the structures from the entrances to the bottoms of the holes showed decarburization, neutral areas and highly carburized areas. The neutral areas were usually found midway between the entrances and the bottoms of the holes.

Another condition which is frequently encountered is a change of surface carbon on the face in contact with the furnace hearth. When using atmospheres of 12.0 per cent CO or under, for instance, the surface in contact with the hearth was often decarburized. This condition was checked quite thoroughly with sections 0.5 inch square by 4 inches long. When the test sections made close contact with the hearth or stainless steel trays, decarburization took place. However, if the material was supported so that the atmosphere had free circulation, this condition did not occur. It does not necessarily follow that decarburization will take place on the surface in contact,
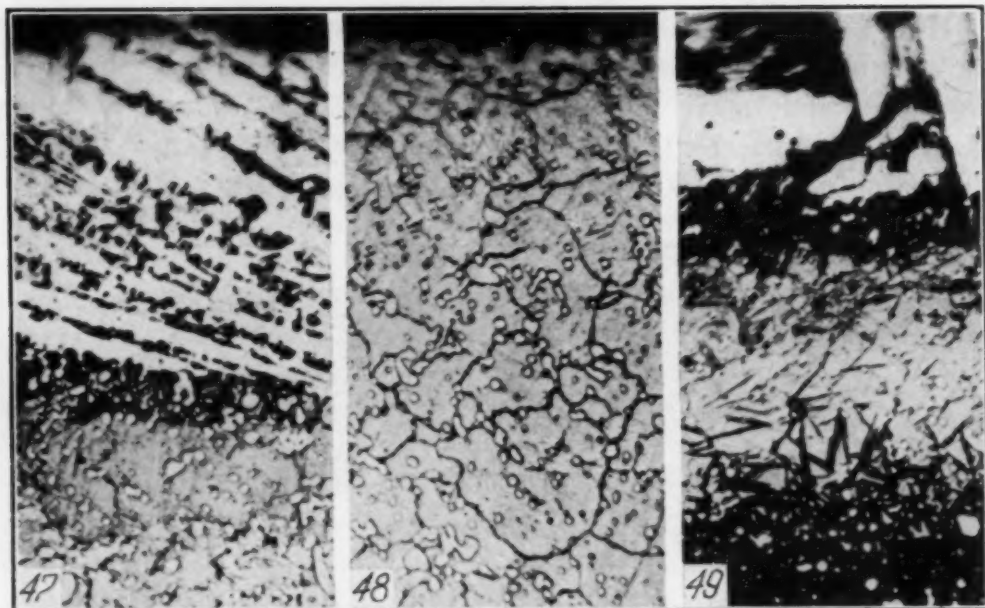
Figs. 47 to 49—Microstructures of Section Coated with Borax During the Super-heat. × 1000. Fig. 47—Oil-quenched 2350 Degrees Fahr., No Draw. Section Where Borax Accumulated During the Superheat Period. Fig. 48—Oil-quenched 2350 Degrees Fahr., No Draw. Section from Which Borax Drained When Being Superheated. Fig. 49—Same as Fig. 47 After Drawing at 1050 Degrees Fahr.

but from the numerous tests which have been made, the indications are that the closer the contact between the material and the hearth, the greater the possibility for decarburization. Fig. 44 shows decarburization on a face which was in contact with the hearth; Fig. 45 shows the microstructure of a decarburized area caused by surface contact.

When the atmospheres have a relatively high percentage of CO (13.0-16.0 per cent) and the material makes close contact with the hearth, excessive carburization is likely to take place. Fig. 46 shows the surfaces of several tools which were treated in a 14 per cent CO atmosphere, and which have wrinkled surfaces due to extreme carburization. The surface of a tool which showed this condition was analyzed for surface carbon by milling five steps of 0.005 inch from the wrinkled face. The results of these carbon analyses follow:

Step 1	Step 2	Step 3	Step 4	Step 5
1.18%	0.86%	0.76%	0.74%	0.72%

The condition of carburization or decarburization on the surface in contact with the hearth may be minimized by placing tools in the furnace on the surface which will have little or no service in actual operation. Both conditions can be eliminated by having the atmos-
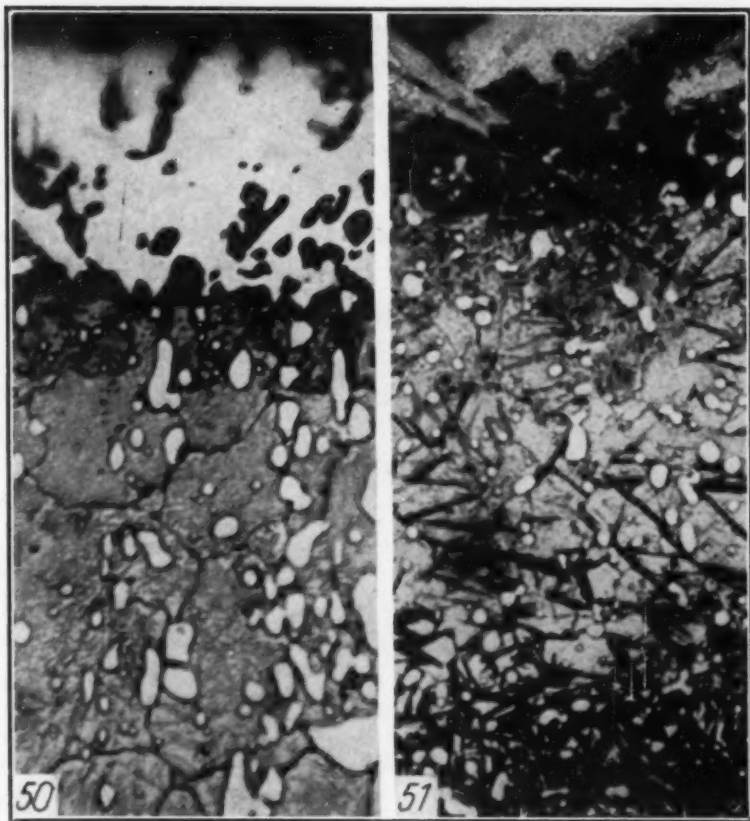
Figs. 50 and 51—Microstructures of Section Treated from a
Carbon Block. × 1000. Fig. 50—Oil-quenched 2350 Degrees Fahr.,
from a Carbon Block—Not Drawn. Fig. 51—Oil-quenched 2350
degrees Fahr., from a Carbon Block—Drawn at 1050 Degrees Fahr.

phere move freely around the work. This can be accomplished by
supporting the tools above the hearth on suitable screens. In sup-
porting tools, extreme precaution must be taken to prevent warpage
due to the high temperatures employed in treating this steel.

Borax is occasionally used in certain types of treating to protect
the surfaces. This method of treating was investigated with a speci-
men 1-inch round by 3 inches long which was preheated in an atmos-
phere of 2 per cent CO to a temperature of 1500 degrees Fahr. (815
degrees Cent.) for a total time of 20 minutes. When preheated, the
specimen was rolled in anhydrous borax, heated to 2350 degrees
Fahr.—total time 7 minutes, and oil-quenched. The borax coating
after treating was removed by sand blasting. The portion of the
specimen where the borax accumulated during the superheating was
highly carburized, while that portion from which borax had drained
showed neither carburization nor decarburization. Fig. 47 shows
the structure where the borax had accumulated during the super-

heating period, and Fig. 48 shows the structure from which the borax had drained. Fig. 49 shows the structure of the carburized area after drawing at 1050 degrees Fahr. and was obtained on the same sample from which Fig. 47 was taken. It is difficult to explain why this specimen showed excessive carburization (Fig. 47) where the borax accumulated, while the area from which the borax drained (Fig. 48) was neutral. The author is of the opinion that the scale which formed during the preheat contained carbides, and when the borax coating was applied and the sample transferred to the high speed furnace, the borax drained toward the base of the specimen carrying with it both scale and carbides. After the specimen had reached a relatively high temperature, the carbides which were in the scale came into contact with the surface, which caused the carburization.

Carbon blocks are frequently used in the heat treating of high speed steels to develop atmospheres which protect the surfaces from excessive scaling and to prevent decarburization. To study the behavior of the surface in treating under these conditions, a specimen 1-inch round by 3 inches long, was treated from a carbon block which had inside dimensions of 1.5 by 4 by 10 inches. The specimen was heated to a temperature of 2350 degrees Fahr. for a total time of 10 minutes, followed by oil quenching. The analysis of the surface carbon in steps of 0.005 inch on the diameter follow:

Step 1	Step 2	Step 3
1.09%	0.78%	0.70%

The analysis of the gas generated in the carbon block was:

$$CO_2—Nil; \quad O_2—Nil; \quad CO—32\text{-}33 \text{ per cent.}$$

Fig. 50 shows the structure of this specimen as oil-quenched, and Fig. 51 shows the structure as oil-quenched and drawn at 1050 degrees Fahr. (565 degrees Cent.) for a total time of 1.5 hours. Fig. 51 is interesting since it shows that some of the retained austenite is partially decomposed by tempering as indicated by the large black acicular martensitic needles.

Blacksmith forges are occasionally used for heat treating certain types of tools. This method of heat treating was investigated with a sample 1-inch round by 3 inches long which was heated in a good bed of coke. An optical pyrometer was used to obtain temperature readings. Naturally this sample was not preheated and was allowed to remain in the forge fire for a total time of 6 minutes. The ap-

proximate temperature of the test according to optical pyrometer readings, under these adverse conditions, was 2380 degrees Fahr. (1305 degrees Cent.). An examination of the surface showed that practically any condition existed; carburization, decarburization, and in certain areas eutectic, which was caused by the fusing of the surface in contact with the hot coke. The Rockwell hardness ranged from C-45 to C-67, and file test showed that some areas were file hard and others were very easily caught.

Before leaving the subject of surface carbon chemistry, a suggested explanation for the carburization which takes place in different

Table VII
The Effect of Atmospheres on Fracture Characteristics and Grain Size

Preheated 2 Per Cent CO Atmosphere—Superheated in an Electric Furnace				
Atmosphere			Fracture Number	Grain Size
CO_2	O_2	CO	Shepherd Standard	Intercept Number
4.0	0.0	15.8	8¾	10.8
4.5	0.0	15.1	9	10.4
5.1	0.0	13.8	9	11.1
5.8	0.0	12.5	9	10.8
6.8	0.0	10.6	8¾	10.6
7.6	0.0	9.4	9¼	11.1
8.8	0.0	7.4	9	10.7
10.3	0.0	4.8	9	10.9
11.5	0.0	2.9	8¾	10.7
12.2	1.1	0.0	9	10.7
10.6	4.3	0.0	9	10.9
9.5	5.6	0.0	9¼	11.2
8.3	7.9	0.0	9	10.2
7.4	9.3	0.0	9	10.8

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—2 per cent CO—Total time 20 minutes.
Superheated 2350 degrees Fahr.—Total time 5 minutes in atmospheres indicated above.
Fracture characteristics and grain size determined in the as-hardened condition.

furnace atmospheres may not be amiss. Primarily there are two chemical reactions operating at the same time. The first is the formation of scale, a strictly oxidizing reaction. It is believed that this oxidation is so rapid in the early stages that it does not materially affect or change the composition of the carbides, but merely attacks the iron or parent metal. The carbides being insoluble in the scale eventually come into contact with the parent metal which is in the austenitic condition and capable of dissolving them; consequently the carburization. In other words, the carburization is a direct result of scaling. This explains to a certain degree why a greater amount of carburization is found with neutral and oxidizing atmospheres; while certain reducing atmospheres cause a lesser amount of carburization. If this theory is correct, then the type of scale formed will also have a direct influence on the amount of carburization. A

loose, porous, flaky, scale will permit the scaling reaction to continue longer than a tight, impervious scale.

The second reaction which takes place is decarburization. It is generally conceded that decarburization may be caused by CO_2, O_2, moisture, hydrogen (moist) and some hydrocarbons under certain conditions. After a certain amount of scale is formed the oxidizing reaction is materially slowed down, and when this occurs the decarburizing action becomes effective. This may be an explanation for the rapid carburization for short times, and the decrease in carburization with longer times; finally decarburization with still longer times.

Table VIII
The Effect of Atmospheres on Fracture Characteristics and Grain Size

| Preheated 2 Per Cent O_2 Atmosphere—Superheated in an Electric Furnace | | | | |
| Atmosphere | | | Fracture Number | Grain Size |
CO_2	O_2	CO	Shepherd Standard	Intercept Number
4.4	0.0	15.5	8¼	10.1
5.8	0.0	12.8	9¼	10.3
6.7	0.0	11.1	9	10.8
7.5	0.0	9.8	9	10.4
8.8	0.0	7.6	9¼	10.7
10.0	0.0	5.0	8¾	10.8
11.1	0.0	3.6	9	10.8
12.7	0.5	0.0	9	11.8
10.9	3.0	0.0	8¾	10.7
8.9	6.3	0.0	9	10.2

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr., 2 per cent CO —Total time 20 minutes.
Superheated 2350 degrees Fahr.—Total time 5 minutes in atmospheres indicated above. Fracture characteristics and grain size determinations made in the as-hardened condition.

The same reasoning can be used to explain why a 10 per cent CO atmosphere decarburizes at 1900 degrees Fahr. (1040 degrees Cent.), and as the temperature is raised, decarburization disappears, and finally, at 2400 degrees Fahr. (1315 degrees Cent.) there is extreme carburization. These conditions are related to the degree of scaling, since as the temperature is increased, the rate of scaling materially increased.

It is recognized that this explanation is contrary to some of our fundamental ideas of the behavior of furnace atmospheres, but from the data it appears plausible.

Part II—Grain Size

It was pointed out in the early part of the paper that the study of fracture characteristics and grain size in high speed steel has been given considerable attention in the literature. Such ambiguous

phrases as "fine silky", "silky", "fine granular", "coarse", "very coarse", "coarse granular", etc., frequently have been used to describe fracture characteristics. In recent years a method has been developed for the classification of fractures, namely, the use of Shepherd fracture standards.

During microscopic examination for grain size, such phrases as

Table IX
Fracture Characteristics and Grain Size—Gas-Fired Furnace

Atmosphere			Fracture Number	Grain Size
CO_2	O_2	CO	Shepherd Standard	Intercept Number
5.7	0.0	7.8	9	10.4
6.7	0.0	6.3	9	10.8
9.1	0.0	3.0	9	10.6
9.8	0.0	2.4	9	10.4

Specimens 1-inch round by 3 inches long—Preheated 1600 degrees Fahr.—Total time 8 minutes.
Same atmospheres for preheating as for superheating.
Superheated 2350 degrees Fahr.—Total time 5 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

Table X
Fracture Characteristics and Grain Size—Oil-Fired Furnace

Atmosphere			Fracture Number	Grain Size
CO_2	O_2	CO	Shepherd Standard	Intercept Number
12.7	0.0	3.5	9¼	10.8
14.1	0.0	2.1	9	10.6
15.1	0.0	0.1	8¾	10.6
15.1	0.3	0.0	9¼	11.0
8.8	9.0	0.0	9	10.7

Specimens 1-inch round by 3 inches long—No preheat.
Superheated 2350 degrees Fahr.—Total time 8 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

"very coarse-grained", "coarse-grained", "slightly coarse", "fine", "extremely fine", etc., have been used to describe structures. Recently the intercept method for the classification or rating of grain size has been developed.

These methods remove much of the ambiguity which formerly existed in classifying fractures and rating grain size, and both were used throughout the experimental work for studying these two physical properties.

1. *Grain Size Obtained When Treating From the Electric, Gas, and Oil-Fired Furnaces*—Many experiments with different types of steel have shown that there is a definite relationship between grain size and other physical properties. In general, the results of these experiments have established that the finer the grain, the higher the

Table XI
Fracture Characteristics and Grain Size

Heat Treatment by Co-operative Firm "A"				
Atmosphere			Fracture Number	Grain Size
CO_2	O_2	CO	Shepherd Standard	Intercept Number
4.0	0.0	16.0	9¼	13.7
6.6	0.0	12.0	9	13.7
9.4	0.0	8.0	9	13.8
11.3	0.0	3.8	9¼	13.6
13.2	0.8	0.0	9	13.3
11.2	3.2	0.0	9	13.8
8.6	6.1	0.0	9	13.7

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—Total time 30 minutes.
Superheated 2350 degrees Fahr. Total time 5 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

Table XII
Fracture Characteristics and Grain Size

Heat Treatment by Co-operative Firm "B"				
Atmosphere			Fracture Number	Grain Size
CO_2	O_2	CO	Shepherd Standard	Intercept Number
7.8	0.0	16.0	9¼	11.9
9.4	0.0	11.6	9	12.4
10.6	0.0	8.2	9	11.9
12.6	0.0	3.8	9¼	11.4
14.6	0.8	0.0	9	11.9
10.9	3.0	0.0	9	12.1
10.6	4.0	0.0	9	11.2

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—Total time 20 minutes.
Superheated 2350 degrees Fahr.—Total time 4 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

Table XIII
Fracture Characteristics and Grain Size

Heat Treatment by Co-operative Firm "C"				
Atmosphere			Fracture Number	Grain Size
CO_2	O_2	CO	Shepherd Standard	Intercept Number
...	...	16.4	9¼	12.2
...	...	12.3	9¼	12.0
...	...	8.0	9½	11.2
...	...	3.5	9¼	12.5
...	0.2	...	9	12.1
...	3.5	...	9¼	11.7
...	6.8	...	9¼	11.5

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—22 to 30 minutes.
Superheated 2350 degrees Fahr.—Total time 3.5 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

strength and the greater the toughness; and vice versa. High speed steel of the 18-4-1 type follows the same general law, and it has been found, other things being equal, that the finer the grain, the higher the strength, the greater the resistance to impact, and the less the

Table XIV

Fracture Characteristics and Grain Size

Heat Treatment by Co-operative Firm "D"

CO₂	O₂	CO	Fracture Number Shepherd Standard	Grain Size Intercept Number
...	...	15.5	9	12.4
...	...	11.5	9	11.8
...	...	8.0	9¼	11.8
...	...	4.0	9¼	12.9
...	...	...	9¼	10.8
...	3.0	...	9	11.8
...	6.0	...	9	10.9

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—Total time 20 minutes.
Superheated 2350 degrees Fahr. Total time 5 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

Table XV

Fracture Characteristics and Grain Size

Heat Treatment by Co-operative Firm "E"

CO₂	O₂	CO	Fracture Number Shepherd Standard	Grain Size Intercept Number
5.4	0.0	14.5	9¼	11.0
6.4	0.0	12.1	9½	10.7
8.6	0.0	7.7	9¼	10.9
10.2	0.0	5.0	9½	11.2
12.6	0.6	0.0	9½	10.4
10.1	4.6	0.0	9¼	10.8
9.0	6.4	0.0	9¼	10.1

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—Total time 20 minutes.
Superheated 2350 degrees Fahr.—Total time 5 minutes.
Fracture characteristics and grain size determinations made in the as-hardened condition.

Table XVI

The Effects of Variable Atmospheres—Variable Time—With Constant Temperature on Fracture Characteristics and Grain Size

CO₂	O₂	CO	Total Time in Superheat—13 Min. Fracture Number Shepherd Standard	Grain Size Intercept Number	Total Time in Superheat—18 Min. Fracture Number Shepherd Standard	Grain Size Intercept Number
4.4	0.0	15.5	9	11.0	8¾	10.6
5.8	0.0	12.8	8¾	12.1	9¼	10.5
7.5	0.0	9.8	9	10.1	9	10.0
8.8	0.0	7.6	9¼	10.6	9	10.5
10.3	0.0	4.8	9	10.3	9¼	11.2
12.7	0.5	0.0	9	10.7	8¾	11.0
10.9	3.0	0.0	9¼	10.9	9	10.9
8.9	6.3	0.0	8¾	11.0	9	10.9

Specimens 1-inch round by 3 inches long—Preheated 1550 degrees Fahr.—2 per cent CO—Total time 20 minutes.
Superheated 2350 degrees Fahr.—as indicated above.
Fracture characteristics and grain size determinations made in the as-hardened condition.
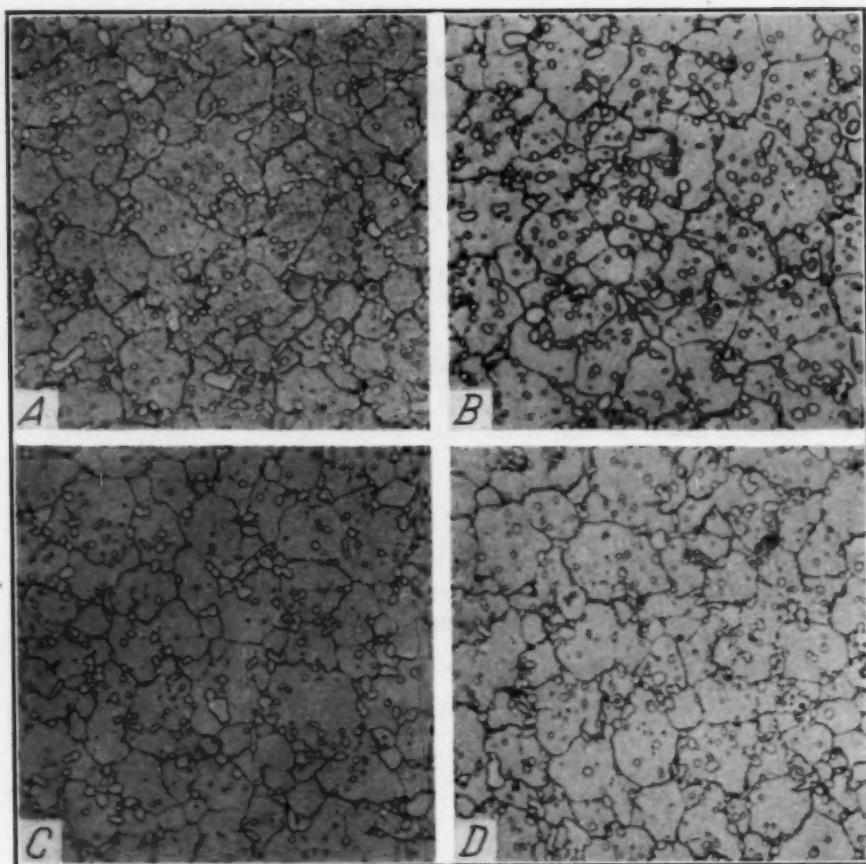
Fig. 52—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2350 Degrees Fahr.—No Hold at Heat. X 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

tendency for the cutting edge to crumble, and with certain types of fine edge tools, the greater the cutting efficiency.

Under subdivision 2 (Part I), the heat treatment from the electric, gas and oil-fired furnaces was fully described. Briefly, the treatment with the controlled atmosphere electric furnace was: Preheated to 1550 degrees Fahr. (845 degrees Cent.), total time 20 minutes, 2 per cent CO; superheated 2350 degrees Fahr. (1290 degrees Cent.), total time 5 minutes, using several different atmospheres. The fracture and grain size determinations were made in the as-hardened condition. The results of this examination are given in Table VII. These data show that neither the fracture characteristics nor the grain size were affected by the type of furnace atmosphere.

The same test was repeated under identical conditions as described above, except the preheating atmosphere was 2 per cent O_2 instead of 2 per cent CO. The results of the study of fracture and

Table XVII

The Effects of Variable Time with Constant Atmosphere and Constant Temperature on Fracture Characteristics and Grain Size

Melt Designation	2½ Min.		5 Min.		10 Min.		15 Min.		20 Min.		30 Min.		40 Min.	
	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size
A	9¼	12.5	9	12.7	9	12.2	9	12.5	9	12.5	9	12.5	9	12.0
B	9¼	13.2	9¼	13.8	9	13.2	9	13.7	8¾	13.0	8¾	13.2	9	12.0
C	9¼	12.1	9¼	12.0	9	11.1	9	11.9	9	12.4	9	10.9	9	10.5
D	9	13.5	9¼	12.5	9¼	11.6	9	11.9	9	11.6	9	11.5	8¾	11.9
E	9	13.1	9¼	13.3	9	12.5	8¾	12.5	9	11.8	8¾	12.4	8¾	11.7
F	9	13.8	9	13.2	9	13.6	9	13.4	9	12.6	9	13.1	9	12.7
G	9¼	12.9	9	13.9	9	13.3	9	13.0	8¾	12.3	9	12.3	9	12.4
H	9	13.7	9¼	12.8	9	13.0	9	13.6	8¾	13.6	9	13.1	8¾	12.8
I	9¼	12.8	9	12.0	9¼	12.8	8¾	12.1	9	12.0	8¾	11.8	8¾	11.4
J	9	13.0	9¼	12.5	9	12.6	9	12.4	8¾	12.0	9	12.1	8¾	12.2

Fracture numbers given above compared with Shepherd Standards.
Grain size given above determined by the intercept method.
Sections 0.5 round by 1 inch long—Preheated 1550 degrees Fahr.—2 per cent CO—15 minutes.
Superheated 2350 degrees Fahr. for the times indicated in a 10.2 per cent CO atmosphere.

Table XVIII

Comparison of Long Soaking Time on Fracture Characteristics and Grain Size When Heated in Gas-Fired Versus Electrically Heated Furnaces

Melt Designation	Gas-Fired Furnace						Electric Furnace—Controlled Atmosphere					
	2 Min.		20 Min.		40 Min.		2 Min.		20 Min.		40 Min.	
	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size	Fracture	Grain Size
K	9	11.1	9	10.9	8¾	10.5	9	11.1	9	10.8	8¾	11.1
L	9	12.3	9	12.5	9	12.7	9¾	13.0	9	12.2	9	12.1
M	9	11.1	8¾	12.0	8¾	10.6	9¾	12.0	8¾	10.7	8¾	11.2
N	8¾	11.3	9	10.8	8¾	11.2	9	11.9	9	11.5	9	10.9
O	9	11.6	9	11.4	8¾	10.9	9¾	12.7	9	12.0	9	10.8
P	8¾	11.5		12.1	8¾	11.1	9	12.0	9	10.7	8¾	11.5
Q	9	11.0	8¾	11.3	8¾	11.2	9	12.3	8¾	11.8	8¾	11.3
R	9	11.3	9	10.8	8¾	11.1	9	11.8	8¾	11.0	9	11.4
S	9	11.1	8¾	10.8	8½	10.8	9¾	11.1	9	11.6	8¾	11.0
T	9	11.1	9	11.0	8¾	10.2	9	11.3	9	11.4	9	11.5
U	9¾	11.7	9	11.9	9	11.5	9	12.3	8¾	11.5	8¾	10.8
V	9	12.3	8¾	11.4	8¾	11.9	9¾	12.2	9¾	10.8	9	11.5

Fracture numbers given above compared with Shepherd Standards.
Grain size given above determined by the intercept method.
Specimens 0.5 round by 1 inch long.
Heat treatment—Gas-fired furnace: Preheated 1600 degrees Fahr.—6.3 per cent CO—Total time 10 minutes.
    Superheated 2350 degrees Fahr.—6.3 per cent CO—Time as above.
    Electric furnace: Preheated 1550 degrees Fahr.—2.5 per cent CO—Total time 15 minutes.
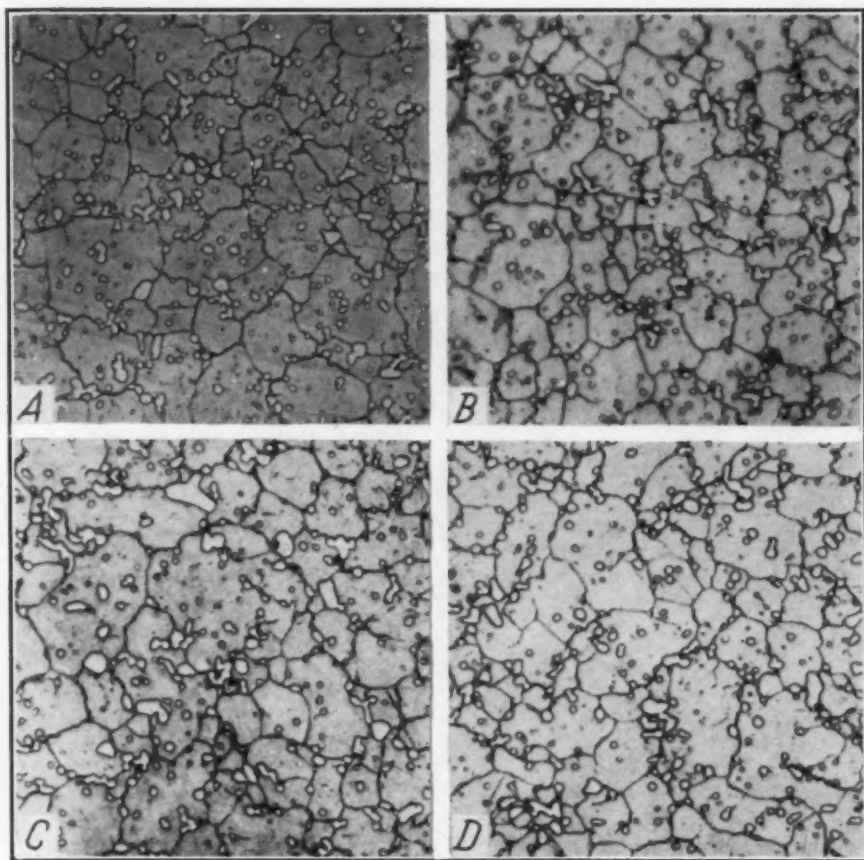   Superheated 2350 degrees Fahr.—11.0 per cent CO—Time as above,

Fig. 53—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2350 Degrees Fahr., Held 5 Minutes at Heat. × 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

grain size characteristics for this treatment are given in Table VIII, which shows that neither of these properties was affected by the type of atmosphere employed.

The two tests made with the controlled atmosphere electric furnace were conducted under conditions commonly encountered in treating this steel and are characteristic of what may be expected with this type of heat treatment. Gas-fired furnaces are also extensively used in treating high speed steel; therefore grain size and fracture characteristics were determined on the specimens treated from this type furnace; and the treatment is fully described under subdivision 2 (Part I).

A summary of this treatment follows: Preheated 1600 degrees Fahr.—total time 8 minutes; superheated 2350 degrees Fahr.—total time 5 minutes. Atmospheres ranged from 7.8 CO to 2.4 per cent
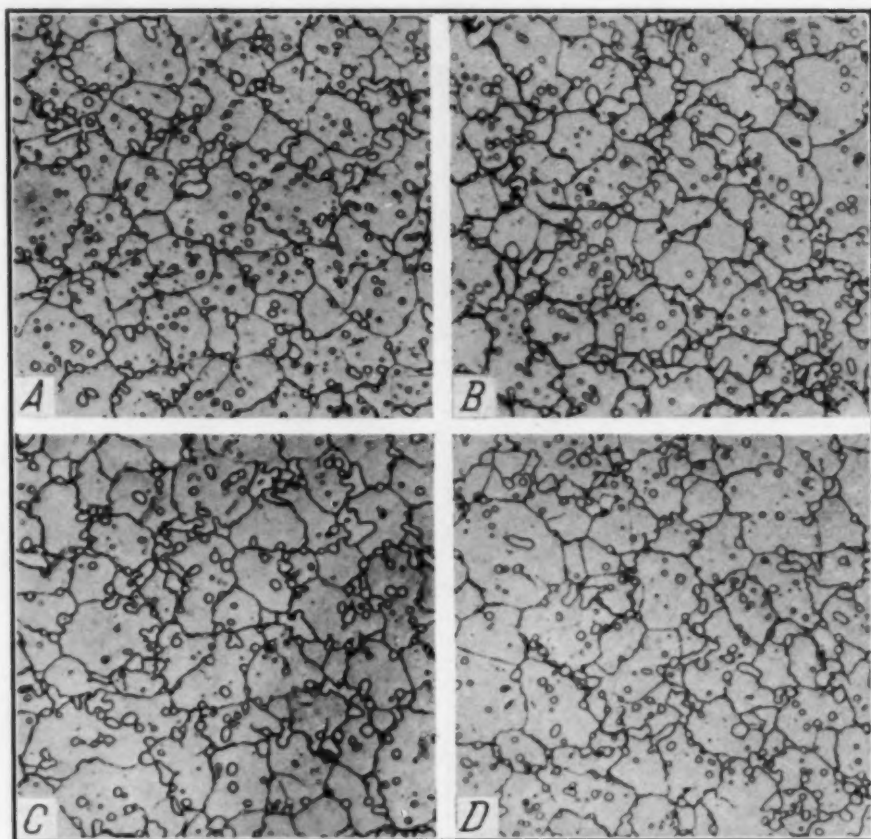
Fig. 54—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2350 Degrees Fahr.—10 Minutes at Heat. × 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

CO. The results of this test are summarized in Table IX, which shows that the grain size and fracture characteristics were identical to those obtained when treating from the electric furnace.

The same examination was made of the specimens treated from the oil-fired furnace, as described under subdivision 2 (Part I). The results are shown in Table X. Comparing the results given in Tables VII, VIII, IX and X, it will be seen that there is no difference in fracture characteristics nor in grain size when treating from any one of the three type furnaces, nor are these properties affected by the many atmospheres employed.

2. *Grain Size Obtained on Confirmative Tests by Co-operative Firms*—The heat treating procedure used by the co-operative firms is fully explained under subdivision 4 (Part I). Both grain size and fracture characteristics were made on all samples, and the results are
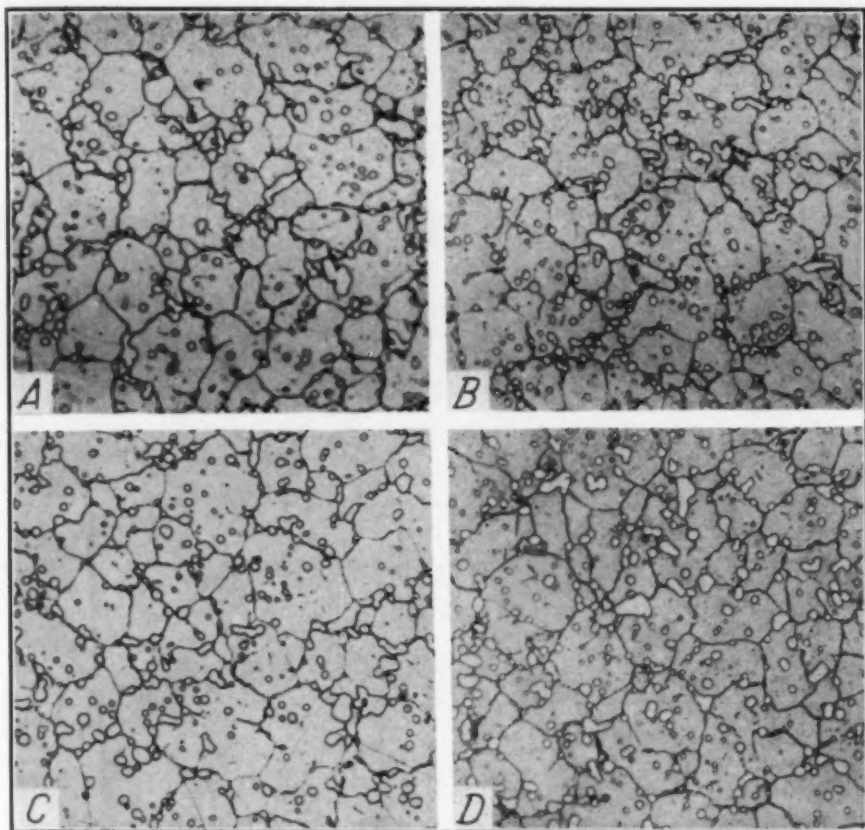
Fig. 55—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2350 Degrees Fahr., Held 15 Minutes at Heat. × 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

summarized in Tables XI to XV, shown on pages 586 and 587.

A study of the results given in these tables show uniform grain size and fracture characteristics, and again it will be noted that there is no indication that furnace atmosphere had any effect on either of these two properties.

3. *Grain Size Obtained with Variable Time, Variable Atmospheres and Constant Temperature*—All of the foregoing tests for the determination of grain size and fracture characteristics were quenched from 2350 degrees Fahr. for normal treating times. To determine what effect longer times at the superheat would have on grain size and to correlate these longer times with atmospheres, a study of these two properties was made on samples treated described under subdivision 6 (Part I). A summary of this treatment follows: Preheated 1550 degrees Fahr.—2 per cent CO—20 minutes; superheated 2350 degrees Fahr. in atmospheres ranging between 15.5 per
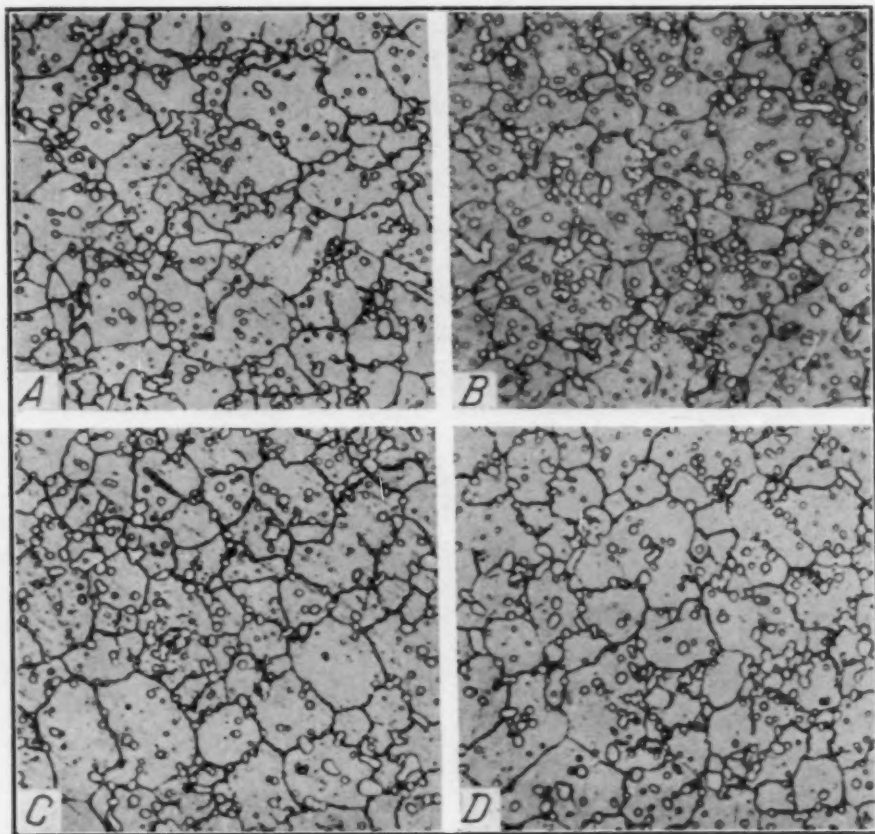
Fig. 56—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2375 Degrees Fahr.—No Hold at Heat. $\times$ 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

cent CO to 6.3 per cent O_2. One group of samples was in the superheat a total time of 13 minutes (approximately 10 minutes at heat). A second group of samples was in the superheat furnace 18 minutes, approximately 15 minutes at heat. The grain size and fracture characteristics obtained with these longer treating times are given in Table XVI. It was surprising to find that neither the time nor the atmosphere had any effect upon the grain size or the character of the fractures.

4. *Grain Size Obtained with Variable Time, Constant Temperature and Constant Atmosphere*—Under subdivision 3 (Part II), it was found that increasing the soaking time in the superheat furnace from a few minutes to 10 or 15 had no effect upon either the grain size or fracture properties. Since we have been repeatedly told that this type of high speed steel showed grain growth on prolonged soaking at a temperature of 2350 degrees Fahr. (1290 de-

Table XIX

The Effects of Variable Time—Variable Atmosphere—Variable Temperature on Fracture Characteristics and Grain Size

Per Cent

Treating Temperature	No Hold at Heat				5 Min. at Heat				10 Min. at Heat				15 Min. at Heat			
	12.0 CO	9.0 CO	1.0 CO	4.0 O_2	12.0 CO	9.0 CO	1.0 CO	4.0 O_2	12.0 CO	9.0 CO	1.0 CO	4.0 O_2	12.0 CO	9.0 CO	1.0 CO	4.0 O_2
Grain Size—Intercept Method																
2200° F.	12.1	11.4	11.1	12.0	12.0	10.9	12.2	10.8	11.9	11.0	11.2	11.3	10.7	11.1	11.9	10.9
2250	11.2	11.5	12.3	12.1	11.7	11.8	11.3	11.0	12.4	11.2	11.9	10.7	11.0	11.2	10.9	11.5
2300	11.3	11.2	11.2	11.0	11.0	10.7	11.1	10.7	11.8	12.2	11.0	11.6	10.0	10.9	10.3	10.4
2350	11.4	11.5	11.7	11.0	11.6	12.0	10.8	11.8	11.5	10.9	11.2	10.6	10.3	11.3	10.8	10.7
2375	11.7	12.2	11.3	11.0	11.5	11.0	11.1	10.4	10.7	10.7	10.5	10.6	9.9	10.5	10.2	9.5
2400	9.0	8.8	9.9	9.4	7.5	7.7	8.5	8.0	7.0	7.6	6.3	4.0	5.5	5.1	6.0	4.0
Fracture Number—Shepherd Standard																
2200° F.	9¼	9¼	9¼	9¼	9	9¼	9¼	9¼	9¼	9¼	9¼	9	9	9	9¼	9
2250	9	9¼	9¼	9¼	9¼	9¼	9¼	9	9	9¼	9	9¼	9¼	9	9	9¼
2300	9¼	9	9	9¼	9¼	9	9¼	9	9	9	9	9	9	9	9	9
2350	9	9	9	8¾	9	9	9	9	8¾	8½	8¾	8¾	8¾	8¾	8¾	8¾
2375	8¾	8¾	8¾	8¾	8¾	8¾	8¾	8½	8½	7½	8½	8¾	8½	8½	8¼	8¼
2400	8¾	8½	8½	8¾	8¼	8¼	8¼	8	7¾	7½	7½	7¾	7	7	7	6¾

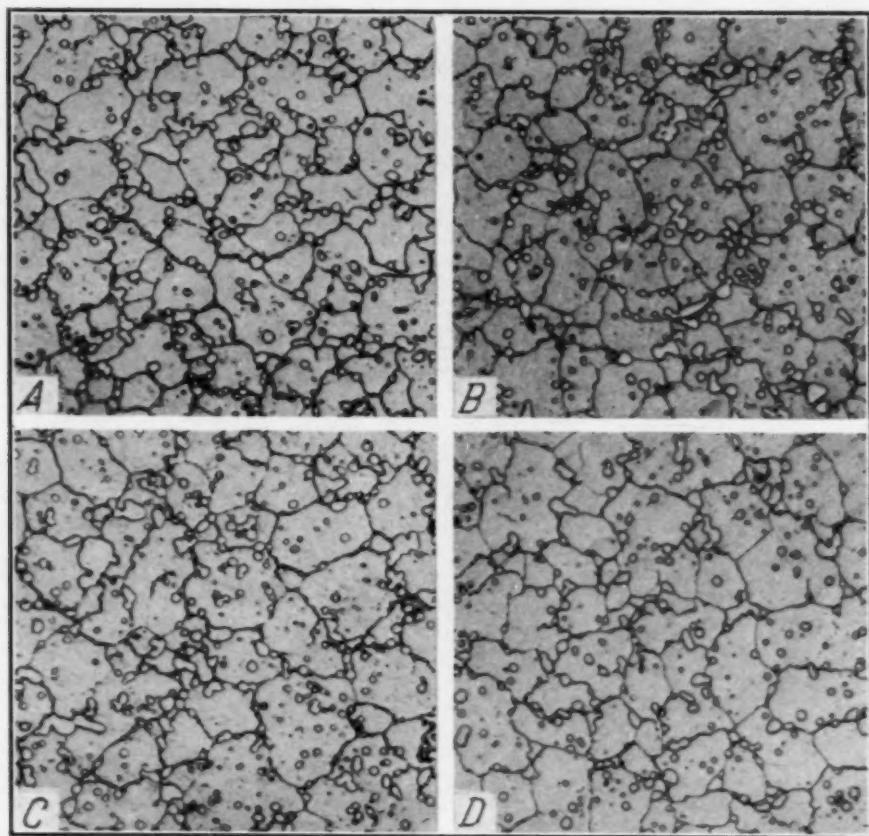Specimens ⅝-inch round by 1 inch long—Preheated 1550 degrees Fahr.—2 per cent CO—Total time 18-20 minutes.

Fig. 57—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2375 Degrees Fahr. Held 5 Minutes at Heat. × 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

grees Cent.), specimens 0.5 inch round by 1 inch long were treated from this temperature for times ranging from 2.5 minutes to 40 minutes at heat. Ten different melts were used in this test. The treatment for these sections is described under subdivision 7 (Part I), and the fracture characteristics and the intercept grain count for these tests are given in Table XVII. These results show that there is no appreciable change in fracture characteristics nor in grain size for the times employed in this test. Both the fracture number and the intercept grain count were the same after a 40-minute soak as for the 2.5 minute period. It must be concluded from these results that this steel is less susceptible to grain growth than is usually supposed.

A portion of this test was repeated in both the electric and gas-fired furnaces. Samples from twelve different melts (exclusive of the ten previous melts) were superheated for periods of 2, 20 and 40 minutes. The treatment in the gas furnace consisted of preheat-
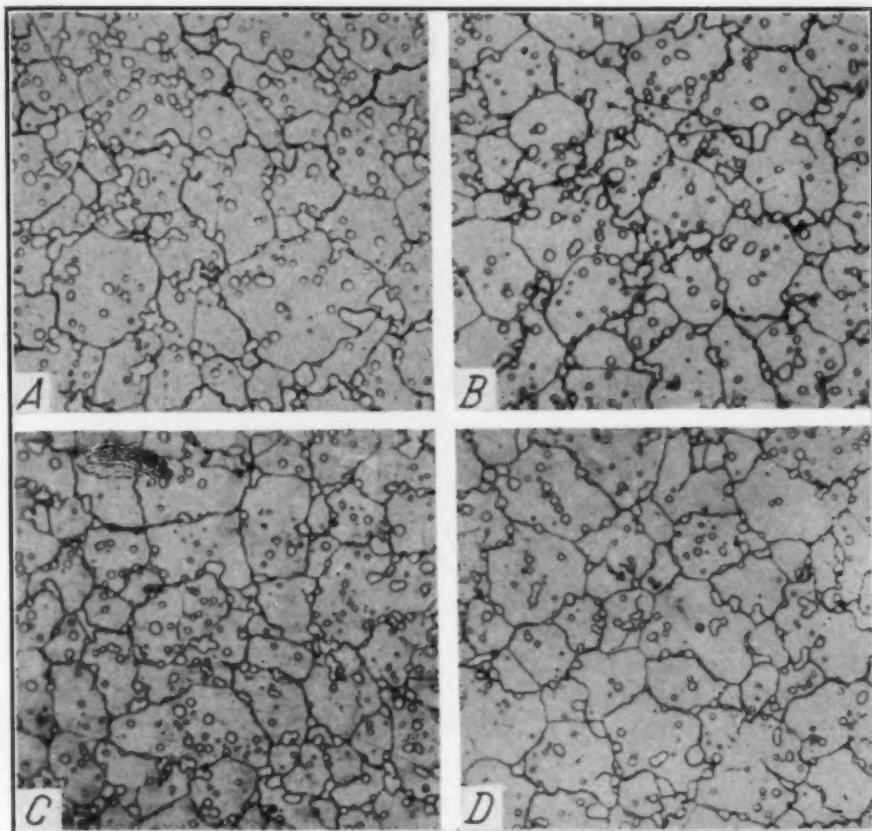
Fig. 58—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2375 Degrees Fahr.—10 Minutes at Heat. × 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

ing the samples to a temperature of 1600 degrees Fahr. for a total time of 10 minutes; superheating to a temperature of 2350 degrees Fahr., holding at heat for the designated times. The atmosphere in both the preheating and superheating chambers of this furnace was 6.4 per cent CO. The treatment in the electric furnace consisted of preheating to a temperature of 1550 degrees Fahr. in a 2 per cent CO atmosphere for a total time of 15 minutes; followed by superheating to 2350 degrees Fahr. in an 11.0 per cent CO atmosphere for the designated times. All sections were oil quenched. The results of these tests are given in Table XVIII. Comparing these results with those given in Table XVII, it will be seen that there is excellent agreement in both fracture and grain size properties. Results given in both Tables XVII and XVIII show that these properties are unaffected by the time at heat or the type of furnace used for the heat treatment.
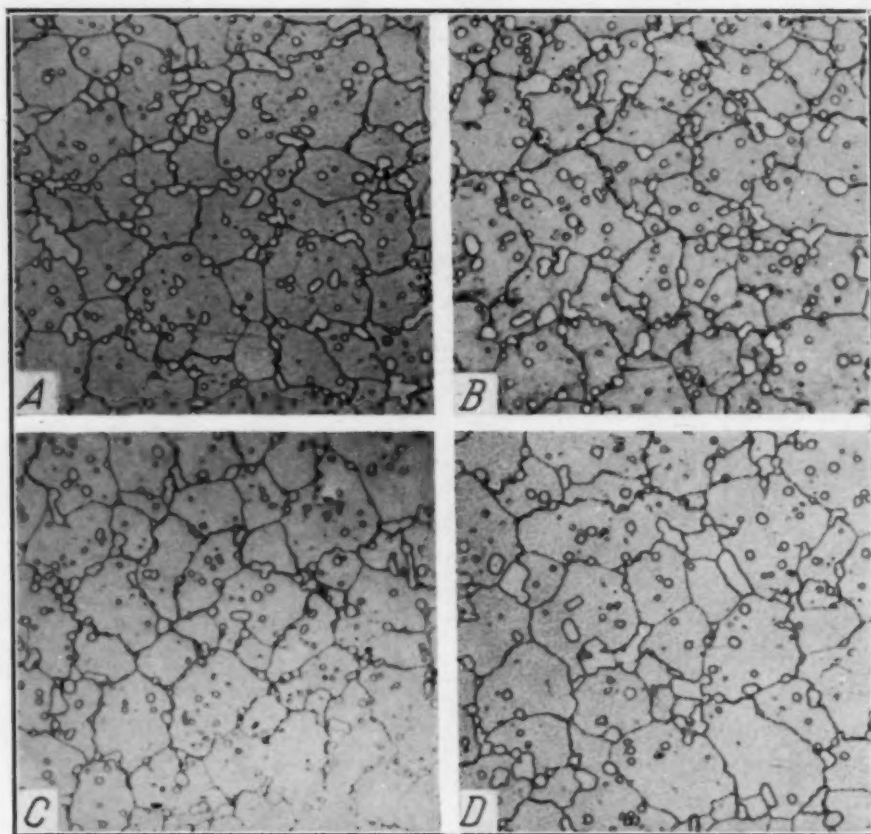
Fig. 59—Influence of Time and Atmosphere on Grain Size. Oil-quenched 2375 Degrees Fahr.—15 Minutes at Heat. × 500. A—Heated in a 12 Per Cent CO Atmosphere. B—Heated in a 9 Per Cent CO Atmosphere. C—Heated in a 1 Per Cent CO Atmosphere. D—Heated in a 4 Per Cent O_2 Atmosphere.

5. *The Effects Upon Grain Size of Variable Time, Variable Temperatures and Variable Atmospheres*—The results of the above tests were contrary to a great deal of the published data as regards fracture characteristics and grain size with prolonged heating and the effect of furnace atmospheres upon these properties. In view of these findings, a more complete study was made of the factors of time, temperature and atmosphere. Ninety-six specimens ⅝-inch round by 1 inch long were machined from a 0.75-inch round bar. All the specimens were preheated to a temperature of 1550 degrees Fahr. in a 2 per cent CO atmosphere for a total time of 15 to 18 minutes. The superheating temperatures ranged from 2200 to 2400 degrees Fahr. Four different atmosphere ranges were employed in the superheating furnace, namely, 11.0 to 12.0 per cent CO, 8.0 to 9.0 per cent CO, 0.50 to 1.50 per cent CO, and 3.5 to 4.0 per cent O_2. Specimens were held at heat in the different atmospheres for zero,
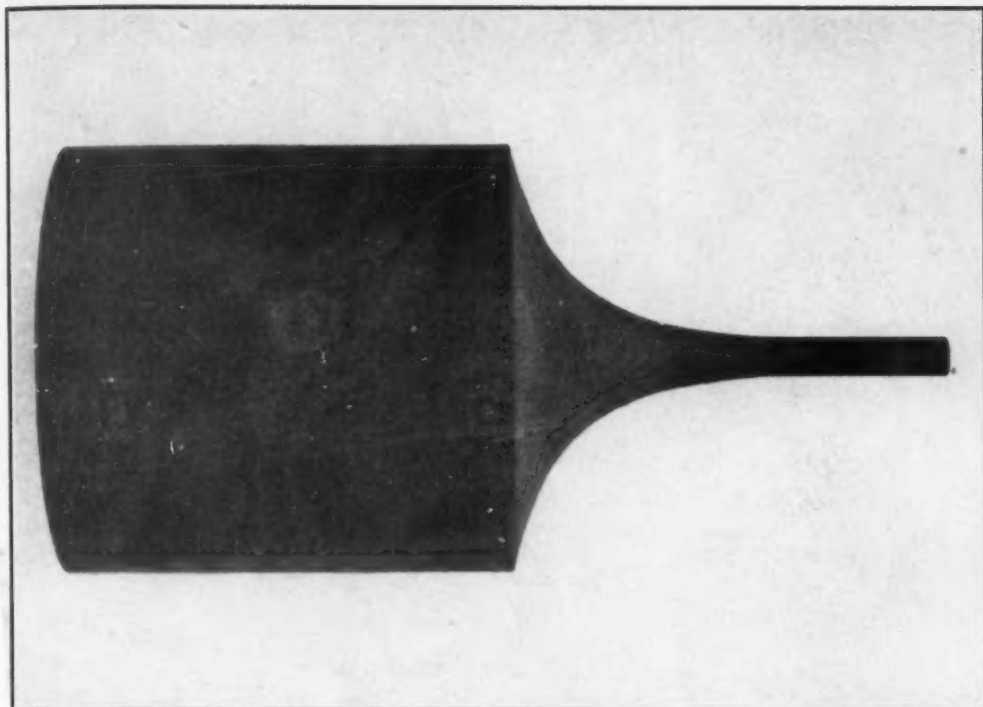
Fig. 60—Unbalanced Test Section. Oil-quenched 2350 Degrees Fahr.—Not Drawn. Actual Size.

5, 10 and 15 minutes. These data are summarized in Table XIX, and a study of this information shows that neither the fracture nor the grain size is affected by any of the factors—time, temperature or atmosphere, until a temperature of 2350 degrees Fahr. is exceeded. At 2375 degrees Fahr., and a holding time of 15 minutes, there is slight indication that grain growth occurs. When treating from 2400 degrees Fahr. a more definite indication of grain growth is evident, when soaking times of ten or fifteen minutes are employed. Another very important observation is that regardless of the time or temperature, the furnace atmosphere did not influence the grain size or fracture characteristics during any of these treatments. These data indicate that the factors of importance in treating this steel are time and temperature, time being secondary so long as the temperatures do not exceed 2350 degrees Fahr. (1290 degrees Cent.). Apparently this type of steel may be held in the temperature range of 2300 to 2350 degrees Fahr. for a considerable length of time without affecting the fracture characteristics or the grain size.

Returning to the results given under surface carbon chemistry, it must be remembered that decarburization occurs rapidly after the soaking time exceeds 15 minutes in an atmosphere of 10 per cent CO.
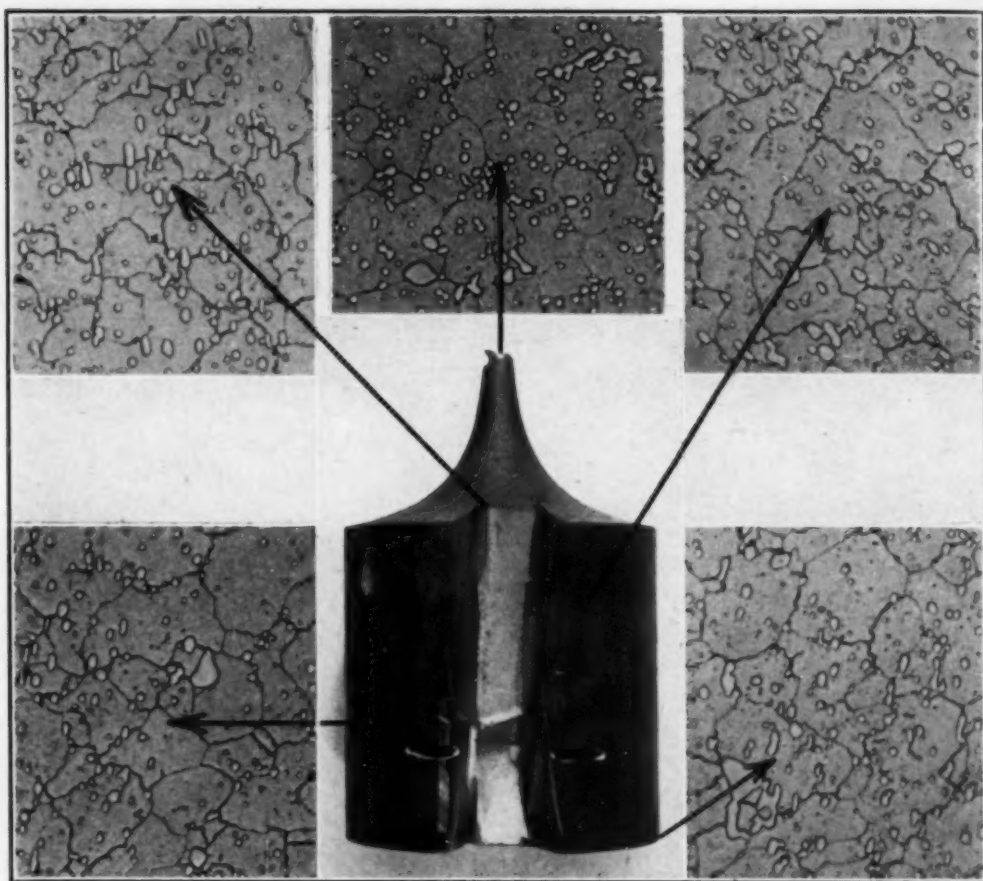
Fig. 61—Photomicrographs Showing Structures of Indicated Positions. × 500.

In other words, increased soaking times will be limited by the type of atmosphere and the temperature of the furnace if excessive decarburization is to be prevented.

From the data given in Table XIX, it is apparent that this steel offers quite a broad field for further investigation as to the effect of both time and temperature upon tool life. According to the author's knowledge of commercial heat treating, very little high speed steel has been treated from temperatures of 2300 to 2350 degrees Fahr. for periods longer than were necessary to bring the tools to heat. Therefore it is possible that better cutting efficiency and longer tool life may be obtained if both time and temperature are further investigated. This problem should be studied by the tool manufacturers, who have at their command efficient methods of testing.

A photographic record at a magnification of 500 diameters has been included to show the structure of this steel treated from temperatures of 2350 and 2375 degrees Fahr. in four atmospheres and
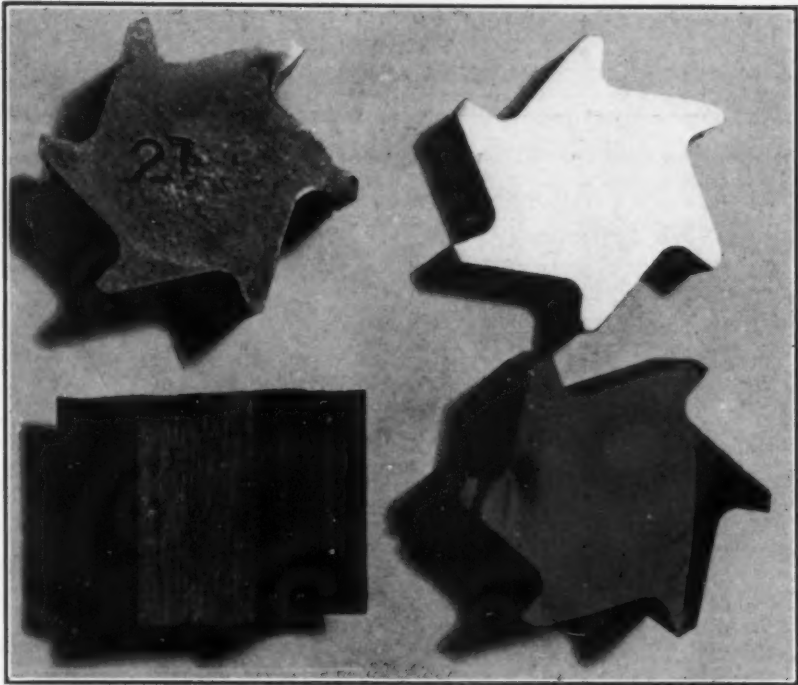
Fig. 62—Test Sections Simulating Reamers. Actual Size.

Table XX
The Results of Grain Size Determination (Intercept Method) on Different Sizes of Bar Stock

Bar Size Inch		Grain Size 2 Minutes at Heat	Grain Size 10 Minutes at Heat
1/8	round	13.6	13.5
1/2	round	13.3	12.7
5/8	round	12.8	12.4
7/8	round	12.1	11.3
1	round	12.4	11.3
1 3/8	round	13.4	12.3
1 5/8	round	12.2	11.2
2	round	12.6	11.3
3	round	12.1	11.5
3 1/2	round	11.6	10.9
1/4	square	13.2	12.8
1/2	square	12.5	11.6
7/8 by 1/2		12.2	11.7
1 by 3/4		12.8	11.6
3 by 5/8		11.8	11.8
4 by 1 1/2		12.8	12.7

Preheated 1550 degrees Fahr.—2 per cent CO.
Superheated 2350 degrees Fahr.—10 per cent CO.

for different soaking periods.

Fig. 52 shows the structure of samples treated from 2350 degrees Fahr. in the different atmospheres and given no soak; Fig. 53 the same condition except for a 5-minute soak; Fig. 54 a 10-minute

Table XXI
Heat Analyses

Subdivision				Per Cent				
	Carbon	Man-ganese	Silicon	Phos-phorus	Sulphur	Chro-mium	Tungsten	Vanadium
1	0.72	0.28	0.20	0.024	0.024	3.79	18.70	1.07
2, 3 and 1*	0.72	0.31	0.26	0.021	0.022	3.74	17.84—	1.12
4, 5 and 2*	0.72	0.30	0.28	0.020	0.020	3.72	17.73	1.12
6 and 3*	0.71	0.26	0.24	0.021	0.021	3.66	18.56	1.10
7 and 4*	0.65	0.26	0.25	0.023	0.023	3.85	18.46	1.11
	0.66	0.25	0.19	0.023	0.025	3.76	18.53	0.97
	0.65	0.27	0.21	0.021	0.027	3.85	−17.85	1.09
	0.71	0.30	0.26	0.020	0.020	3.80	18.46	1.09
	0.73	0.27	0.24	0.020	0.020	3.66	18.58	1.11
	0.65	0.30	0.27	0.022	0.023	3.92	17.95	1.18
	0.67	0.26	0.26	0.022	0.021	3.60	18.16	1.13
	0.73	0.28	0.27	0.022	0.021	3.71	18.31	1.12
	0.71	0.30	0.26	0.021	0.027	3.86	18.03	1.15
	0.71	0.30	0.25	0.022	0.021	3.75	17.70	1.13
8	0.73	0.31	0.26	0.022	0.021	3.91	18.34	1.12
	0.73	0.31	0.28	0.022	0.022	3.70	18.07	1.13
	0.71	0.31	0.23	0.021	0.022	3.66	18.43	1.13
	0.71	0.27	0.25	0.021	0.021	3.66	18.43	1.13
	0.71	0.28	0.26	0.021	0.021	3.67	18.50	1.13
	0.72	0.30	0.26	0.020	0.020	3.78	18.42	1.07
	0.74	0.30	0.26	0.020	0.020	3.78	18.43	1.06
9 and 13	0.71	0.29	0.24	0.020	0.019	3.88	18.52	1.05
12	0.72	0.30	0.26	0.020	0.019	3.80	18.29	1.12
14	0.71	0.31	0.25	0.020	0.019	3.74	17.96	1.10
	0.72	0.29	0.20	0.020	0.020	3.84	17.75	1.07
	0.71	0.29	0.26	0.019	0.020	3.78	18.27	1.13
4*	0.71	0.21	0.15	0.025	0.017	3.88	18.66	1.13
	0.72	0.27	0.24	0.022	0.018	3.90	18.49	1.08
	0.73	0.29	0.25	0.020	0.027	3.85	18.23	1.15
	0.71	0.28	0.21	0.024	0.026	3.81	17.66	1.10
	0.73	0.30	0.22	0.022	0.026	3.82	17.80	1.13
	0.60	0.30	0.25	0.021	0.027	3.81	17.66	1.13
	0.71	0.30	0.22	0.022	0.026	3.82	17.93	−1.12
	0.77	0.29	0.26	0.021	0.029	3.75	18.67	1.08
	0.73	0.30	0.28	0.020	0.021	3.82	18.15	1.11
	0.73	0.29	0.24	0.020	0.020	3.92	17.80	1.13
	0.70	0.35	0.46	0.029	0.023	4.03	18.01	1.13
	0.73	0.29	0.18	0.021	0.018	2.76	17.70	1.14
5*	0.71	0.31	0.22	0.022	0.020	3.76	18.16	1.10
6*	0.74	0.29	0.20	0.024	0.024	3.89	18.69	1.12
	0.73	0.23	0.23	0.022	0.020	3.72	17.85	1.08
7*	0.71	0.29	0.28	0.020	0.021	3.68	18.30	1.11
	0.71	0.26	0.24	0.021	0.021	3.66	18.56	1.10
	0.71	0.31	0.27	0.020	0.021	3.77	18.46	1.09
	0.71	0.28	0.25	0.022	0.020	3.81	18.22	1.15
	0.71	0.33	0.29	0.021	0.021	3.82	17.90	1.10
	0.71	0.29	0.25	0.022	0.021	3.82	18.43	1.12
	0.71	0.30	0.27	0.021	0.021	3.84	17.85	1.08
	0.71	0.29	0.27	0.021	0.021	3.84	18.10	1.09
	0.70	0.29	0.21	0.024	0.026	3.81	17.66	1.10
	0.72	0.24	0.23	0.021	0.020	3.67	17.79	1.05
	0.71	0.23	0.24	0.022	0.020	3.70	17.81	1.07
	0.71	0.24	0.24	0.020	0.020	3.74	17.82	1.06
	0.71	0.28	0.20	0.021	0.019	3.73	17.88	1.07
	0.71	0.29	0.22	0.022	0.018	3.79	18.06	1.08
	0.71	0.30	0.17	0.021	0.017	3.76	17.72	1.17

*Refers to subdivisions of Part II of this paper.

soak; and Fig. 55 a 15-minute soak. Figs. 56 to 59 inclusive show the structures when treated from a temperature of 2375 degrees Fahr. under the same conditions of time and atmospheres as were enumerated for Figs. 52 to 55 inclusive.

6. *Grain Size on Test Pieces with Differential Sections*—It is readily recognized that the larger majority of tools are composed of

unbalanced sections. Two different shapes were used to study the effect of temperature upon sections of unbalanced design. The first of these consisted of a test piece which had a 2-inch round base and a $\frac{3}{16}$-inch round tip, the base having a length of 2 inches and the tip a length of 1 inch. A generous fillet was allowed between the 2-inch base and the $\frac{3}{16}$-inch tip. This unbalanced section was preheated to 1550 degrees Fahr. in a 2 per cent CO atmosphere, and superheated to 2350 degrees Fahr. in a 10 per cent CO atmosphere. The $\frac{3}{16}$-inch round tip reached the superheating temperature in about $1\frac{1}{2}$ minutes, while it required 10 minutes for the 2-inch round base to come to heat. After both base and tip were at heat, the section was given an additional 5 minutes soak. A photograph of this section after oil quenching is shown in Fig. 60.

Different sections of this test piece were examined for fracture and grain size properties. The fracture characteristics of both the heavy and light sections were identical, namely, fracture No. 9. The grain size on the small section, according to the intercept method was 10.4, and the base showed an intercept number of 9.9. Fig. 61 shows the sectioned test piece, together with photomicrographs at 500 diameters taken from various parts of this test.

The second shape, which simulated a reamer, was used to determine the effect of time and temperature on heavy and light sections. Bars 1.25 inches round were turned to 1-inch round; the 1-inch round bars were then fluted with six splines approximately $\frac{3}{16}$ inch deep. Test samples 1 inch long from these fluted sections were heated to 2350 degrees Fahr. for periods of 2, 6, 10 and 15 minutes in an atmosphere of 10 per cent CO. After oil treating both the fracture and the grain size were found to be the same on the thin and heavy portions of this section, and as in previous tests, the grain and fracture characteristics were unaffected by time in the superheat. Fig. 62 shows several views of this shape.

7. *Grain Size on Various Sizes of Bar Stock*—Test samples were cut from bars ranging in section from 0.25 to 3.5 inches. The various sizes includes squares, flats and rounds. Test pieces from these different sizes were oil treated from 2350 degrees Fahr. (1290 degrees Cent.). One group was held 2 minutes and a second group was soaked 10 minutes at the superheat. The intercept method was used to determine the grain size, the results of which are given in Table XX. The study of these data requires no further comment.

8. *The Effect of Preheating Time on Grain Size*—One of the

questions frequently discussed in the treating of high speed steel is the effect of preheating time and temperature on final grain size. Several tests were made on 0.5-inch square bars which were machined from ⅝ inch square. The preheating temperature in each instance was 1550 degrees Fahr., and the atmosphere employed was 2.0 per cent CO. The times held at the preheating temperature ranged from no soak to 20 minutes, followed by superheating to 2350 degrees Fahr. (1290 degrees Cent.) for a total time of 5 minutes. Throughout these tests, all factors were constant except the time in the preheat furnace. An examination of these specimens for both grain size and fracture characteristics indicated that time in the preheating furnace does not affect the final grain size. Another indication that the preheating time does not materially affect the final grain size was the results obtained on the sections which were carburized from 1600 degrees Fahr. (870 degrees Cent.) for a total time of 6.5 hours, and for a total time of 11 hours. Both fracture and grain size after oil treating these samples from 2350 degrees Fahr. (1290 degrees Cent.) were identical with samples taken from the same bar of steel, the latter having been given the normal preheating and superheating cycle.

Summary

The most important phases of this work can be summarized as follows:

1. During normal heat treating with a freely moving atmosphere some carburization may be expected.

2. Atmospheres which carburize for short time heating periods may eventually cause decarburization if the time in the superheat is sufficiently prolonged.

3. The carburized zone cannot be seen under the microscope in the as-quenched condition, but must be drawn at a temperature of 950 to 1150 degrees Fahr., after which it will appear as partially retained and partially transformed austenite.

4. Retained austenite can be broken down by repeated drawing. The amount produced on the surface in normal heat treating can be broken down as a rule by a second draw at a temperature of 1050 degrees Fahr. However, the rate at which the retained austenite breaks down at any one temperature depends upon the carbon concentration. This is an additional explanation why double drawing is

reported to produce tools which are more efficient and have better cutting properties than those which have been given a single tempering operation.

5.   A study of grain size and fracture characteristics indicates that this steel is not susceptible to grain growth when treated from 2350 degrees Fahr. or lower.

6.   The composition of the furnace atmospheres used in these commercial heat treating furnaces did not affect the grain size nor fracture characteristics.   The only factors influencing grain growth as determined by the intercept method and the Shepherd fracture standards are time and temperature, time being of secondary importance when temperatures of 2350 degrees Fahr. or lower are used.

7.   Since this steel resists grain growth far better than has been previously supposed, it invites further interesting experiments to see if added tool efficiency can be had with the use of longer soaking times and even slightly higher hardening temperatures.

ACKNOWLEDGMENT

References

1. F. W. Taylor, "On The Art of Metal Cutting."   An address published by the American Society of Mechanical Engineers.   Third Edition, p. 52.
2. Sam Tour, "The Temperature Atmosphere Problem and High Speed Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 21, 1933, p. 269.
3. Arthur Phillips and M. J. Weldon, "Contributory Effects of Furnace Atmospheres in Grain Size of Molybdenum High Speed Steel," TRANSACTIONS, American Society for Metals, Vol. 23, 1935, p. 886.
4. James P. Gill, "High Speed Steel—Carbide Segregate and Grain Size," TRANSACTIONS, American Society for Metals, Vol. 24, 1936, p. 735.
5. B. F. Shepherd, "The P-F Characteristics of Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 22, p. 979.
6. R. W. Snyder and H. F. Graff, "Study of Grain Size in Hardened High Speed," Metal Progress, April 1938, p. 377.
7. B. H. DeLong and F. R. Palmer, "What Happens When High Speed Steel is Quenched," TRANSACTIONS, American Society for Steel Treating, Vol. 13, p. 420.
8. Morris Cohen and P. K. Koh, "The Tempering of High Speed Steel," TRANSACTIONS, American Society for Metals, Vol. 27, p. 1015.

DISCUSSION

Written Discussion: By N. B. MacLaren, vice-president, Brown & Sharpe Manufacturing Co., Providence, R. I.

Mr. Schlegel has presented a very interesting paper and one which should furnish material for considerable thought and discussion. He is to be congratulated for the time and effort which must have been put into such an investigation. In this discussion I will not attempt to enter into a technical consideration of the various points brought out but will confine myself to some observations in practice.

In connection with the portion of the paper dealing with grain size, particularly the conclusions on the influence of variable time on grain size of high speed steel heated at 2350 degrees Fahr. (1290 degrees Cent.), may I state that the conclusions are contrary to our experience. Tests made on induction melted disks 2½ inches in diameter by ½ inch thick showed that both time and atmosphere have a definite effect on grain size when hardened at 2350 degrees Fahr. (1290 degrees Cent.). Using an atmosphere analyzing about 7 per cent CO specimens increased in grain size from 14.7 to 12.4 when the time was varied from four to thirty minutes. When an oxidizing atmosphere was employed, a specimen hardened for 30 minutes at 2350 degrees Fahr. (1290 degrees Cent.) had a grain size of 11.4 as compared with 12.4 for a reducing atmosphere.

In this connection it may be well to discuss the author's statement in paragraph 3 wherein he states: "Today the majority of tools made from high speed steel are treated from a temperature range of 2300 to 2350 degrees Fahr. (1260 to 1290 degrees Cent.)." It is our belief that better cutting performance and higher red hardness result when tools are hardened from a higher range, for instance, 2350 to 2375 degrees Fahr. (1290 to 1300 degrees Cent.). In some cases we know that 2400 degrees Fahr. is used. It would have been well if the author had included results for a slightly higher temperature.

It is also interesting to note that samples treated in both oxidizing and reducing atmospheres show an increase in carbon on the surface up to about 16 per cent CO. We find in actual practice it is advisable to use only a reducing atmosphere in the heating of 18-4-1 in order to protect the surface of delicate tools and particularly form cutters which are ground on the face of teeth only. We have found in general that a range of 8 to 12 per cent CO is quite satisfactory.

The time at temperature, we find, gives us the best results when they are heated through. A prolonged heating, after this point has been reached, does no particular good but does rough the surface.

As manufacturers of all types of cutters, we, at this time, are not ready to subscribe to all the conclusions cited in this paper. The author has rekindled an interest in the treatment of high speed steel and I am sure in the near future much activity will be noticed in attempting to verify and check the many interesting facts which were obtained by the author.

Written Discussion: By John F. Wyzalek, chief metallurgist, Hyatt Bearings Div., General Motors Corp., Harrison, N. J.

The paper presents data on surface conditions of heat treated high speed

steel which are very interesting. Mr. Schlegel offers evidence which supports the previous belief of others that under certain heating conditions the carbon content of the surface of high speed steel tools was raised during the hardening operation, thereby explaining higher surface hardness of unground tools with better performance in some applications. The test results point towards the possibility of improved tool performance through intelligent use of controlled furnace atmospheres in hardening high speed steels. An elaboration of the paper through extension of tests using atmospheres more in line with actual practice might also serve to guide properly those who may not be in position to use modern furnace equipment which provides the means to control furnace atmospheres.

Regarding the author's findings that the 18-4-1 high speed steel used in his test indicates it is not susceptible to grain growth at temperatures up to 2350 degrees Fahr. (1290 degrees Cent.) confirms recent findings of others. It prompts one to raise the question whether the general belief to the contrary should not be revised, which probably is predicated on experience of some years ago when perhaps the general run of such high speed steels had an entirely different grain character. In view of present 18-4-1 high speed steels offering an opportunity of fine grain even with longer soaking time, as Mr. Schlegel appropriately states, it will be interesting to watch developments to see whether increased tool efficiency can be accomplished through this means.

Written Discussion: By J. G. Morrison, metallurgist, Landis Machine Co., Waynesboro, Pa.

Mr. Schlegel is to be highly commended for his exhaustive investigation of furnace atmospheres relative to their effect on the alteration of the surface chemistry which occurs in the treatment of 18-4-1 steel. The statistical nature of his approach to this subject is indicative of a thorough awareness of the difficulties attendant to such an investigation. While it has been known for some time that 18-4-1 steel tends to absorb carbon at the surface during heating in the usual atmospheres employed at 2350 degrees Fahr. (1290 degrees Cent.), it has remained for Mr. Schlegel to conduct his comprehensive research and change the belief resulting from more or less meager observation to one of conviction.

The accumulation of all the analytical "surface" carbon data, as illustrated by the Fig. 11, convincingly establishes the tendency of 18-4-1 steel to absorb carbon during heating for hardening at 2350 degrees Fahr. (1290 degrees Cent.) under widely varying atmospheres as regards the percentage of CO or O_2. This characteristic of 18-4-1 steel is perhaps one of the contributing factors for the general use and usefulness of this type of high speed steel since the time of Taylor and White to the present day.

We have observed the wrinkled surfaces illustrated in Fig. 46, which are indicative of such a degree of carburization as to cause incipient fusion. Using a semi-muffle oil-fired furnace, the atmosphere of which contained about 1.5 per cent CO if paper were placed on a pure nickel tray and flat surfaced 18-4-1 steel placed thereon, the wrinkled surface resulted after a superheat of 2350 degrees Fahr. (1290 degrees Cent.).

As a further example of the great surface activity which may maintain

in the 2350 degrees Fahr. (1290 degrees Cent.) furnace if flat 25 per cent chromium-20 per cent nickel trays are used and flat surfaced 18-4-1 steel placed thereon quite the reverse action occurs on the contact surface in that decarburization results. There appears to be a reaction between the Cr_2O_3 of the tray and carbon present as a soot or, with the carbon in the high speed steel, or both. Cr_2O_3 in the presence of carbon above 2180 degrees Fahr. (1195 degrees Cent.) decomposes into metallic chromium and oxygen. This nascent oxygen is an active decarburizer, and a preheated specimen ¼ by 1 by 2 inches placed in the superheat for as little as 2 minutes may show a total decarburization of 0.0015 inch. If one places a small specimen as above on a sheet of low carbon steel and hardens it from 2350 degrees Fahr. (1290 degrees Cent.), there is no noticeable decarburization. However, if a little pure Cr_2O_3 is placed on the tray and the specimen placed thereon, the contact surface of the high speed steel will decarburize.

Mr. Schlegel's explanation of the mechanism of carbon absorption is plausible but we would question that the solution of the carbides alone accounts for the carbon pick-up. To know just what happens at the surface during the sojourn in the superheat we would probably have to know something about the catalytic effects of the relatively cold high speed steel surface and mass action effects as the surface undergoes continued change with increase in time. Our own conception, none-the-less conjectural, is as follows:

When 18-4-1 steel is first placed in the superheat, whether preheated or not, some oxide is present on the surface. In the early stages of heating some oxidation of the surface continues but, relatively, it is not extensive. The matrix appears most susceptible to oxidation, particularly at structural discontinuities such as at carbide borders. Due to the relatively cold surface of the steel when first placed in the superheat some soot may be deposited on the surface because of the breakdown of the furnace gases under possible catalysis. The slight fuzz one may sometimes observe about the edges of samples shortly after placing in the superheat is suggestive of a soot. The early oxidation of the matrix carbon and of some of the carbide carbon may be a source of the absorbed carbon. Postulating the presence of a soot on the surface the carbon preponderates and we may have the reaction $CO_2 + C = 2\ CO$. This nascent CO is in immediate or almost immediate contact with the steel surface and a rapid carburization ensues in the accepted manner.

As the temperature of the steel surface increases, sooting diminishes and finally ceases. Oxidation then proceeds even in a 10 per cent CO atmosphere. This results in an increasing loss of surface by oxidation or scale formation. The oxidation or scaling of the surface is almost compensatory to the diminishing carbon which occurs at the surface once oxidation predominates. Hence the reason a considerable time is required before there occurs any considerable loss in carbon (in the first 0.0025 inch of surface) below that originally contained in the steel. The carbides, at least the larger ones, oxidize relatively slowly and those carbides which are present in the scaled zone probably serve as a partial deterrent to the continued oxidation of the steel surface. In a 10 per cent CO atmosphere there appears to be no regeneration of the high carbon exterior once oxidation of the surface predominates.

That the carburizing action is arrested with a subsequent decarburizing

action is perhaps a fortunate circumstance. If carburization were to continue fusion would occur as in pack hardening at 2250 degrees Fahr. (1230 degrees Cent.) and above. The wrinkled surface above referred to is a case in point. Here, due to the furnace atmosphere being blocked off from the contact surface, the carburizing action continued to fusion.

The foregoing explains why samples containing sharp projections heated in a 10 per cent CO atmosphere do not absorb as much carbon on the sharp points as on a flat surface. The more rapid heating of the sharp points and the greater turbulence of the furnace gases in their vicinity hinder the deposition of any considerable soot. Oxidational changes may come into play earlier but the sharp projections having absorbed less carbon are less susceptible to the rapid oxidation which proceeds on those surfaces which have absorbed a considerable amount of carbon.

When the atmosphere contains about 2 per cent or more O_2 the oxidation of the sharp projections is so rapid that fusion results. In this case there appears to be a continuous formation of the high carbon exterior on the projections. This high carbon zone may or may not be due to the solution of the carbides of the fused zone.

The foregoing explanation in no way detracts from this excellent paper, which is indeed a valuable contribution to the all too meager literature on high speed steel furnace atmospheres.

Written Discussion: By J. P. Gill, chief metallurgist, Vanadium-Alloys Steel Co., Latrobe, Pa.

The writer has read Mr. Schlegel's paper with great interest and it is certainly an excellent contribution to the knowledge which exists on the heat treatment of high speed steel. The part of the paper which discusses the surface carbon chemistry will undoubtedly excite additional experimental work on the part of a number of investigators. I do not feel that, in general, the data which Mr. Schlegel has presented are at variance with the experimental data which others have presented. I feel that any one who would conduct the experiments identically as they have been conducted by Mr. Schlegel would obtain similar data.

The chemical reactions which take place at the surface of high speed steel during heat treatment must be most complex and undoubtedly many theories could be offered as to the nature of the surface reactions. Possibly a plausible explanation of carburization from oxidizing atmosphere would be that the CO_2 present in the gases upon initially contacting the surface of the steel caused the formation of a slight amount of scale, thereby producing carbon and CO which carburized the surface under the scale at the same time the scale was forming. As the thickness of the scale increased, as it probably would on increasing the time at temperature, the carbon and CO gas could not contact the solid steel and decarburization began to take place. Undoubtedly the gases on contacting the surface of the steel are materially changed in composition and probably one cannot know the mechanics of carburization until we can learn how the gases break up on contacting the steel. It should also be mentioned that gases which may not carburize a plain carbon steel might possibly carburize a steel containing alloys which have an extremely high affinity for carbon, such as tungsten and vanadium.

In reference to grain size of high speed steel, the author has apparently not made the same detailed investigation of this part of the paper as with the surface chemistry. He makes practically no comment as to the restraining influence on grain growth of the segregate and the segregate distribution. Certainly grain size in high speed steel depends on a large number of factors and its control does not appear to be as simple as the author has indicated. A casual study of the literature shows many inconsistencies in the deductions that have been made on this subject. Mr. Tour in his paper on "The Temperature Atmosphere Problem in High Speed Steel", published in 1933, noted that with change in atmosphere there was not only a difference in grain size but even a difference in the apparent point of fusion of the segregate. There is no question but what Mr. Tour's experiments were accurately conducted just the same as I think have been the experiments of Mr. Schlegel, but the deductions were probably incorrect.

The speaker, on trying to make similar experiments, placed thermocouples in the center of the specimen and it was found that when the temperature control was from the inside of the specimen the atmosphere did not affect the size of the grain unless it affected the temperature of the specimen.

It is regrettable in the present paper that a greater variation in methods of heating were not used, such as the salt bath or the Sentry block, or by using gas of a single composition, such as air alone, pure CO_2 gas and pure CO. By using the extremes the effect of atmospheres as it affects the temperature of the specimens becomes distinctly more noticeable.

Several years ago, we purchased three or four different brands of 0.70 per cent carbon 18-4-1 high speed steel on the open market and have done so again within the last few weeks. Amongst these brands of steel was that manufactured by the company which Mr. Schlegel represents. This procedure was followed so that if there did exist variations in manufacture that would contribute to restraining grain growth, it would be noticed. In a number of experiments which we have made and in using material of similar segregate distribution, we did not find any material difference in these several steels in their reaction to grain growth. Some of the specimens were subjected to hardening in the Hayes furnace having an atmosphere of about 9 per cent CO. After preheating at 1550 degrees Fahr. (845 degrees Cent.) and transferring to the Hayes furnace at a temperature of 2350 degrees Fahr. (1290 degrees Cent.) and holding for 10 minutes the resulting grain size is shown in micrograph Fig. 1 of this discussion. An adjacent piece of the bar was held 10 minutes in a salt bath at the same temperature of 2350 degrees Fahr. (1290 degrees Cent.) and the grain size which resulted is shown in the photomicrograph Fig. 2. Another piece of the same material was held in a Sentry block at 2350 degrees Fahr. (1290 degrees Cent.) for 5 minutes with a grain size as indicated in photomicrograph Fig. 3, and another piece was held in the Sentry block at the same temperature of 2350 degrees Fahr. (1290 degrees Cent.) for 20 minutes with the grain size shown in photomicrograph Fig. 4. Thus, using three radically different methods of heating, but all supposedly at the same temperature, we certainly obtained quite a variation in grain size.

From past experiments which we have made on this subject, I feel certain that had we measured the temperature not with a thermocouple on the outside

of the specimen but with a thermocouple on the inside of the specimen, we would have found that there was a temperature variation and that the variation in temperature was responsible for the differences in grain size noted.

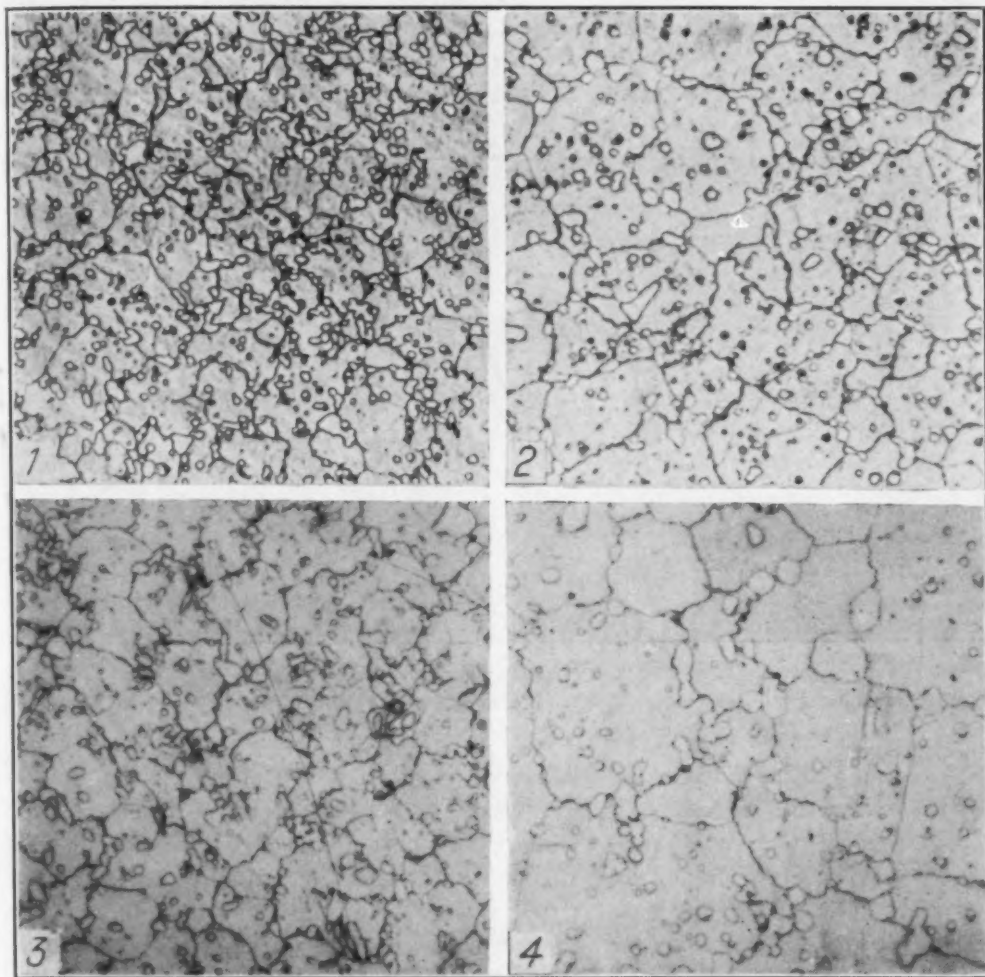The pronounced effect of the segregate on controlling grain size in high

Fig. 1—18-4-1 Steel Preheated at 1550 Degrees Fahr. and Transferred to a Hayes Furnace at 2350 Degrees Fahr. Fig. 2—Same as Fig. 1 except Piece was Transferred to a Salt Bath at 2350 Degrees Fahr. Fig. 3—Same as Fig. 1 except Piece was put in Sentry Block at 2350 Degrees Fahr. Fig. 4—Same as Fig. 3 except Piece was held in Sentry Block at 2350 Degrees Fahr. for 20 minutes.

speed steel is so obvious that it hardly seems necessary to comment on it. The photomicrographs, Figs. 1 to 4, were taken from specimens approximately 1 inch in diameter and all of which were held at 2350 degrees Fahr. (1290 degrees Cent.) but now we take a disk ½ inch thick from a bar 5 inches in diameter and we hold it in a semi-muffle furnace for only 5 minutes at a much lower temperature, namely, 2300 degrees Fahr. (1260 degrees Cent.), and an extremely large grain results. This is indicated in photomicrograph Fig. 5. Select other areas in the same specimen and examine them for grain size and there exists a distinct mixture of very large and very small grains, depending wholly upon the distribution of the segregate in the different areas.

Photomicrograph Fig. 6 is from the same specimen that photomicrograph Fig. 5 was from, treated only at 2300 degrees Fahr. (1260 degrees Cent.) and shows both a very large grain and a comparatively small one.

The photographs of Fig. 7 of the fractures of a 1-inch round treated from 2350 degrees Fahr. (1290 degrees Cent.) for 10 minutes and of the disk taken from the 5-inch round treated to only 2300 degrees Fahr. (1260 degrees Cent.) show a radical difference in the fracture grain size; the small round being in the vicinity of about 9½ on the Shepherd test and the large round only about
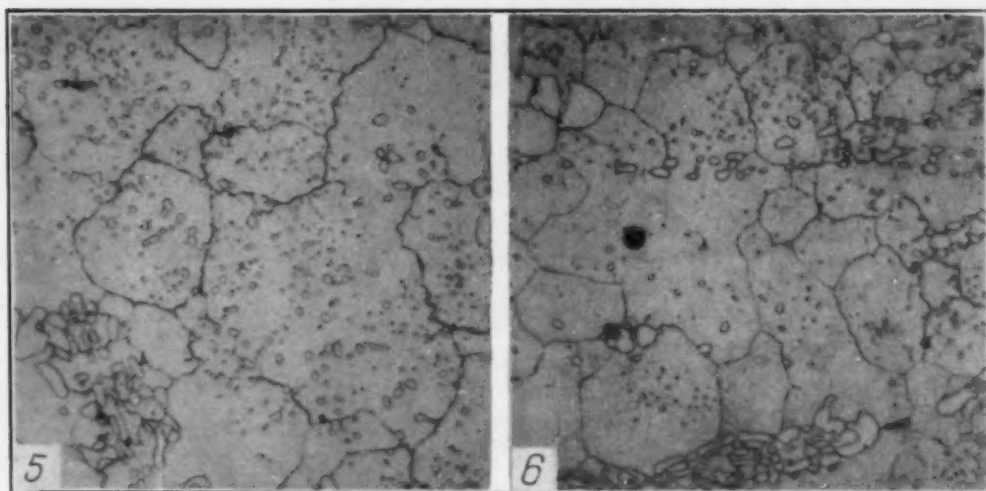

Fig. 5—18-4-1 Steel Held 5 Minutes in Semi-Muffle Furnace at 2300 Degrees Fahr.
Fig. 6 Same as Fig. 5 Showing Both Large and Small Grain Size.

7¾ on the Shepherd test. The difference in the coarseness of the fracture is not because of the difference in grain size but because of the difference in the distribution of the segregate. In large sections the segregate is usually so coarse that it affects materially the appearance of the fracture and certainly in large sizes the fracture is not a true indication of the actual grain. For this reason we do not feel that the Shepherd fracture standards are applicable to high speed steels.

A few generalizations can be made in reference to grain size of 18 per cent tungsten high speed steel that are of interest. We have compared the grain size of specimens heat treated at 2350 degrees Fahr. (1290 degrees Cent.) in semi-muffle furnaces with the grain size in specimens treated at the same temperature in similar type furnaces some ten years ago and it is rather interesting to note that in every case where we have been able to make comparisons the grain size in the specimens more recently treated is always smaller. I think this can be wholly attributed to the fact that heat treaters of high speed steel have universally become conscious of the effect of atmospheres while ten years ago this was not at all true. We note today that samples of high speed steels treated by almost everyone show a finer grain at similar temperatures than they did some ten years ago.

The restraining effect of the carbide segregate on grain growth has been intently studied and it does seem that there is a certain range of temperatures

whereby, after maximum solution of the segregate has been obtained, that part of the segregate not dissolving has a restraining influence on grain growth and thereby lessening the effect of time. When time does affect greatly grain growth the temperature must be sufficiently high so that there is a high solution of the carbides. As to what the limits of these temperatures are is not of simple definition as the degree of solution of the carbides is dependent on their size
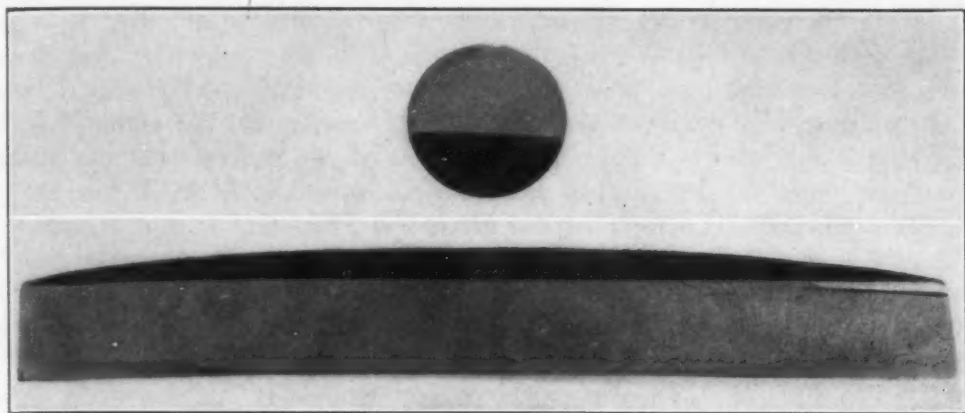

Fig. 7—Photograph of the Fractures of a 1-Inch Round and a 5-Inch Round Treated at 2350 and 2300 Degrees Fahr. Respectively.

and distribution. As to why the author did not note the effect of carbide distribution on grain size in the samples heat treated can be explained upon several bases. First—Undoubtedly the size range was not sufficiently wide and, second, oftentimes there is considerable difference in the carbide distribution between different bars of the same size, depending upon what part of the ingot they have been rolled.

It would appear that there is an approximate maximum solubility for the carbides at each temperature and after this maximum solubility has been reached, holding the material an increased length of time is not likely to materially affect the physical characteristics of the steel. This would seem to preclude the possibility that long time holding of high speed steel at some temperature would be likely to be materially beneficial and always with the possibility of being highly detrimental because of the surface reactions.

The author spoke of a temperature of 2300 to 2350 degrees Fahr. (1260 to 1290 degrees Cent.) as being that generally used for treating 18-4-1 high speed steel. Many tool manufacturers using controlled atmosphere furnaces use a temperature of 2375 degrees Fahr., some even slightly higher.

Written Discussion: By J. E. McCambridge, metallurgist, U. S. Navy Yard, Philadelphia.

I wish to congratulate Mr. Schlegel for his very thorough and comprehensive investigation into the surface carbon chemistry and grain size of heat treated 18-4-1 high speed steel. As everyone who has heat treated a high speed lathe tool knows, it is customary to grind off the "skin" before attempting to obtain a hardness reading on the quenched tool, but it has remained for Mr. Schlegel to demonstrate to us that this skin is due to carburization rather than to decarburization, which was the popular belief.

Mr. Schlegel's tests have indicated that the grain growth in 18-4-1 is very slow, even with extended time, at temperatures of 2350 degrees Fahr. (1290 degrees Cent.) and that grain growth does not really start until a temperature of 2400 degrees Fahr. (1315 degrees Cent.) is reached. The maximum grain size as determined by the intercept method, on approximately 225 specimens heat treated from 2350 degrees Fahr. (1290 degrees Cent.), under varying conditions of atmosphere and at times ranging from 2 to 40 minutes is 10.0, while the minimum is 13.9. This is a very narrow range of grain sizes and would tend to indicate that any 18-4-1 high speed steel, heat treated in atmospheres ranging from approximately 16 per cent CO to 4 per cent O_2 at a temperature of 2350 degrees Fahr. for a normal time, would fall within it.

This is not always the case, however, as steels of this type may attain grain sizes differing quite widely from those noted above, when treated under similar conditions. A survey of the grain sizes, by the intercept method, of 147 lathe tool noses gave widely varying results. These tools were preheated at 1600 degrees Fahr. (870 degrees Cent.) and then held at 2350 degrees Fahr. (1290 degrees Cent.) for four minutes and quenched in oil. While 94 of the tool noses fell within the range of 10 to 14 grain size, the remaining 53 varied from 8.5 to 20.2. A résumé of the number of tool noses in the various grain sizes follows:

No. of Tool Noses	Grain Size (Intercept Method)
5	Above 8 to and including 9
19	Above 9 to and including 10
21	Above 10 to and including 11
26	Above 11 to and including 12
26	Above 12 to and including 13
21	Above 13 to and including 14
11	Above 14 to and including 15
8	Above 15 to and including 16
2	Above 16 to and including 17
2	Above 17 to and including 18
0	Above 18 to and including 19
1	Above 19 to and including 20
1	Above 20 to and including 21

Complementing the wide range of grain sizes obtained by heat treating various 18-4-1 tool steels under practically identical conditions is the fact that some of these steels will show widely varying conditions within the same tool. The tool noses referred to above were obtained by heat treating approximately four inches of a ½ by 1 inch bar, 12 inches long. After being ground and run, 1 inch was cut from the end of the tool, which was then reground and run a second time. Under such conditions of heat treatment, it might be supposed that the second tool nose, if varying from the first, would show a finer grain size. This actually occurred in 47 of the 73 pairs investigated. Three of the pairs showed no change in grain size, while in the remaining 23 pairs, the grain size of the second tool nose was coarser than that of the first one. The maximum coarsening of the first tool nose over the second was 9.2, while the maximum refining was 4.8.

It is apparent from these results that time and temperature are not the only elements which influence the grain growth of 18-4-1, and that in spite of the very thorough investigation made by Mr. Schlegel, a very considerable field is open for further exploration.

Written Discussion: By M. J. Weldon, metallurgist, Sanderson Works, Crucible Steel Co. of America, Syracuse, N. Y., and L. S. Bergen, associate director of metallurgy and research, Crucible Steel Co. of America, N. Y.

The author is to be highly congratulated on a splendid contribution to the voluminous literature on 18-4-1 high speed steel.

It is only too well appreciated that this type of steel may be very susceptible to carbon absorption under certain conditions of heat treatment which are by no means established within precise limits. In many cases, the carburized surface areas of high speed steel may have been diagnosed as over-heated or decarburized by people unfamiliar with high speed steel. However, it should be remembered that over-heated structures are sometimes obtained when the steel has been heated to unusually high hardening temperatures over 2450 degrees Fahr. (1345 degrees Cent.). The high speed steel expert can distinguish between these two types of structure, although considerable experience is necessary to do so.

One of the outstanding properties of modern 18-4-1 high speed steel is its

Table I
The Effects of Variable Temperature and Time on Austenitic Grain Size
(Intercept Method)

Superheating Temperature	Time at Heat (Minutes)	Steel A (Arc Melted)	Steel B (Induction Melted)	Steel C (Induction Melted)
2350 Degrees Fahr.	1	15.6	13.6	12.8
	2	15.2	13.6	13.4
	5	15.6	14.2	12.4
	10	15.8	14.4	13.0
	15	15.6	14.4	13.0
	30	14.2	13.6	13.6
	45	14.6	13.6	13.4
	60	14.0	12.0	13.0
2400 Degrees Fahr.	1	13.0	13.0	12.0
	2	13.6	12.6	12.0
	5	13.8	12.6	10.4
	10	13.0	11.8	11.0
	15	12.0	11.2	10.6
	30	13.0	11.2	10.0
	45	11.0	11.0	10.0
	60	8.0	6.6	7.0
2450 Degrees Fahr.	1	11.0	9.8	10.0
	2	10.2	7.8	9.6
	5	8.8	6.2	7.6
	10	5.5	4.6	5.0
	15	4.5	3.6	3.6

Chemical Analyses

	C	Mn	P	S	Cr	W	V
Steel A	0.71	0.27	0.029	0.020	4.05	18.07	1.10
Steel B	0.74	0.33	0.029	0.020	3.92	18.39	1.17
Steel C	0.68	0.25	0.022	0.024	3.67	17.80	1.01

Specimens—Steel A—0.500 inch round—1½ inches long
—Steel B—0.500 inch round—1½ inches long
—Steel C—1 inch x ½ inch—1½ inches long

Legend—Specimens preheated in gas-fired, muffle furnace at 1550 degrees Fahr. Time—30 minutes.
Superheated in muffle furnace under slightly reducing conditions (2/3 per cent CO).
Each specimen oil-quenched from superheat and cooled to room temperatures.
Grain determinations made on sections cut by a thin abrasive wheel across the widths and midway between the ends of the 1½ inch lengths.
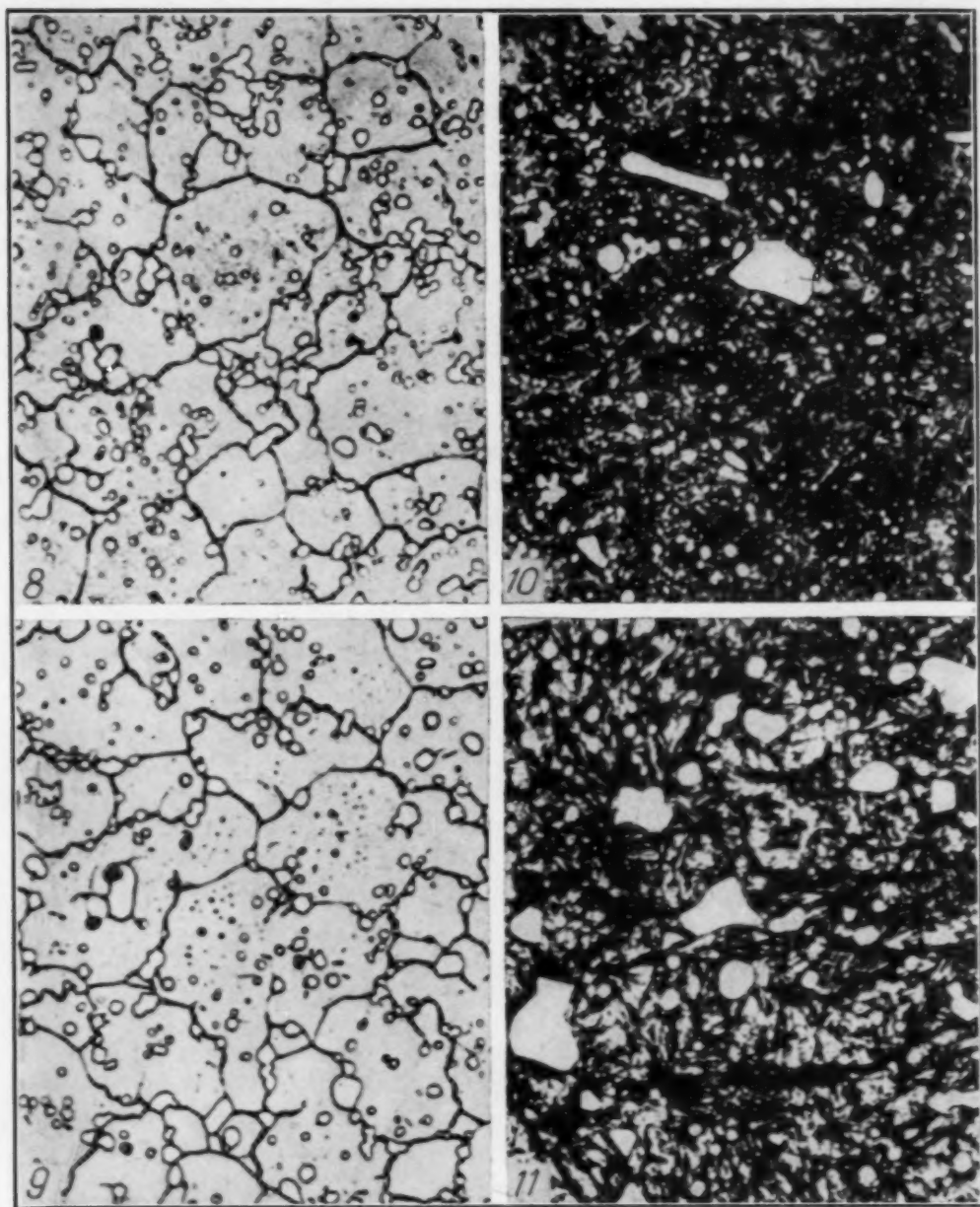
remarkable resistance to grain growth within the broad hardening ranges employed by industry. Mr. Schlegel's results indicating that the grain size of this grade is not coarsened after long holding periods at 2350 degrees Fahr. (1290 degrees Cent.) confirm what has been known for some time. Any belief that extended holding at 2350 degrees Fahr. (1290 degrees Cent.) caused grain growth is undoubtedly a carry-over from the old empirical days when the tool was put into a hot furnace and held until a "sweat" began to appear. Longer holding under these conditions would cause grain growth because the furnace temperature was actually greater than 2350 degrees Fahr. (1290 degrees Cent.)

The introduction of the modern high speed steel heat treating furnace apparently improved control but did not alter the retention, by some, of old empirical "laws." Since the author's data are all on induction melted material, the figures given in Table I are of interest because they compare arc and induction melted 18-4-1 and show that the arc melted material is at least equal to the induction melted. However, although the conditions at 2350 degrees Fahr. (1290 degrees Cent.) are perfectly understood, the effect of higher hardening temperatures has not been completely clarified. Mr. Schlegel indicated that abrupt grain growth occurs at 2400 degrees Fahr. Typical results obtained by us at this temperature, as shown in Table I, are not in agreement with this finding. The results obtained at 2450 degrees Fahr. (1315 degrees Cent.), as shown in this Table, are also of interest, as Mr. Schlegel did not give any figures on temperatures as high as this, although such heating temperatures are sometimes used in industry.

Nevertheless, the grain size should not be regarded as a final criterion of the properties of the steel unless consideration is also given to the carbide appearance and the matrix structure as developed by a nital etch on tempered specimens. This point is illustrated by Figs. 8, 9, 10 and 11 of this discussion showing structures of Steel A. One specimen was held for one minute, the other for 30 minutes at temperature. After this treatment, both samples had the same intercept grain size, although, as shown, the structure after tempering was not the same. In other words, the grain size alone does not tell the whole story.

Written Discussion: By Burns George, metallurgical engineer, Vanadium-Alloys Steel Co., Latrobe, Pa.

The result of Mr. Schlegel's tests on atmospheres in high temperature furnaces which show carburization of high speed steel in any furnace, regardless of atmosphere, are apt to be quite misleading to the average heat treater of this material. Such results may cause the hardener to infer that type of atmosphere is no longer of importance, since he can expect to have a high carbon surface on his tools in any case.

Experience is sufficient proof of the mistake for such assumption. Obviously surface appearance alone will make the use of some atmospheres very undesirable. Mr. Schlegel shows that carburization may occur in atmospheres containing as much as 9 per cent oxygen but we feel the scaled and sweated surface which may result from such an atmosphere may be very objectionable to say nothing of the size change which may take place under these conditions.

The carburization which takes place as revealed by this paper may not be as damaging as first study would indicate. For the most part it is superficial carburization existing in highest degree to a depth of 0.002 inch as revealed by the graphs. The results of the second and third cuts of 0.002 inch each show it is possible to prevent carburization above 1 or 2 per cent of the general carbon content. Assuming a steel containing 0.70 per cent carbon, the 2 per cent carburization would only amount to 0.014 inch or an increase to 0.714 per cent, which is certainly nothing to worry about.

The writer wonders if Mr. Schlegel has studied the effect of the various atmospheres as to their tendency to carburize to depths greater than 0.002 to 0.0075 inch. Some results of the writer's tests made at various times in the

past would indicate that carburization of 18-4-1 high speed steel may occur quite deeply with some atmospheres. The following results would indicate there is considerable importance to controlling the atmosphere in order to prevent carburization from going beyond the shallow depths noted in this paper.

**Type of Furnace Used—Hayes Controlled Atmosphere
Type of Gas—Pyrofax**

Specimen Number	Manometer Air	Setting Gas	Surface Carbon Per Cent	Cross Section Carbon Per Cent
1	3	2½	1st 0.005 inch—0.86 2nd 0.005 inch—0.80 3rd 0.005 inch—0.76 4th 0.005 inch—0.74 5th 0.005 inch—0.72	0.72
2	3	1½	1st 0.005 inch—0.78 2nd 0.005 inch—0.75 3rd 0.005 inch—0.75 4th 0.005 inch—0.75 5th 0.005 inch—0.73	0.725
3	3	1	1st 0.005 inch—0.78 2nd 0.005 inch—0.73 3rd 0.005 inch—0.71	0.71

Written Discussion: By A. H. d'Arcambal, consulting metallurgist, Pratt and Whitney, Division Niles-Bement-Pond Co., W. Hartford, Conn.

Some years ago we received reports from the field that such tools as taps and multiple thread cutters gave longer life on certain jobs when furnished as cut thread tools than was the case with similar tools furnished with ground threads. At that time we ran tests on samples of high speed steel given the usual hardening treatment, finding that these samples picked up from 10 to 20 points of carbon on the surface during the hardening operation. This is the first time we have seen any published information bearing out our findings.

We also found in the old days that high speed steel soaked at the hardening heat developed a pronounced grain growth together with a coarse fracture, especially where fuel fired furnaces were employed. It would appear from Mr. Schlegel's paper that high speed steel as manufactured today is of a better quality than that of some years ago, considering that the grain does not coarsen to any great extent even with pronounced soaking. Nevertheless we would like to issue a word of warning: Do not return to your respective shops at the conclusion of this meeting and issue instructions to have all your high speed steel tools soaked for a long period of time at the hardening temperature, else you are liable to find yourself in trouble due not only to excessive scaling but also the production of inferior cutting tools due to increased brittleness as a result of this treatment.

Oral Discussion

SAM TOUR:[1] In the papers by Mr. Morrison and Mr. Schlegel, there has been brief mention of the molybdenum high speed steels. Approximately two

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[1]Vice-president and chemical and metallurgical engineer, Lucius Pitkin, Inc., New York.

years ago, in studying the subject of the soft skin on molybdenum high speed steels, I became convinced that most of the soft skin encountered when using highly reducing atmospheres was due to retained austenite and not decarburization. This is in line with Mr. Schlegel's and Mr. Morrison's findings of surface carbon pick up.

It seems that the principal distinction between molybdenum high speed steel and the 18-4-1 is that the austenite formed due to carburizing of the surface of the molybdenum high speed steels is more stable than that on the 18-4-1 steels. It is possible to give a double or a treble tempering treatment at the usual tempering temperatures of 1050 degrees Fahr., to a surface carburized 18-4-1 steel and break down the austenite skin and obtain good hard surface layers. The molybdenum high speed steels develop an austenitic skin of such stableness that it does not break down at the usual tempering temperatures even on a second or a third tempering treatment.

A metallographic determination that the soft skin on molybdenum high speed steel is austenite and not ferrite is not so simple as Mr. Schlegel says. Many metallurgists have a tendency to say it is decarburization. By retempering such a molybdenum steel at a higher temperature the austenitic skin will break down and develop martensite. However, the core is over-tempered and is ruined. The austenitic layer transforms to martensite at 1200 to 1250 degrees Fahr. but the body of the steel is softened.

The molybdenum high speed steels require control of the furnace atmosphere to prevent excessive carburization of the surface. Attempts to use more and more reducing atmospheres with smoke and carbon in the furnace give excessive carburizing that is more difficult to cope with than slight decarburization from the less reducing atmospheres.

Molybdenum high speed steels seem to be more active toward carbon than the 18-4-1 steels. They pick up carbon faster and they lose carbon faster. If they are heated for too long a time, the excessive carbide layer which forms initially is eliminated and decarburization results. Proper control of the atmosphere results in a satisfactory surface on molybdenum high speed steel.

Author's Reply

The author appreciates the numerous comments received and would like to take this opportunity to thank the discussers for their interest and timely remarks.

From the many discussions it is apparent that the subject of grain size is in an unstable and chaotic condition. Mr. MacLaren has found a slight coarsening of the grain when the time was increased from 4 to 30 minutes in a 2 per cent CO atmosphere at 2350 degrees Fahr. (1290 degrees Cent.). Mr. McCambridge has observed different grain sizes in a large number of lathe tools, which undoubtedly were manufactured from different brands of steel, when treated under identical conditions. Mr. Wyzalek has reported that this type of steel does not show grain growth when treated from 2350 degrees Fahr. (1290 degrees Cent.) or lower. Messrs. Weldon and Bergen have reported that 18-4-1 high speed steel resists excessive grain growth at temperatures of 2400 degrees Fahr. (1315 degrees Cent.), with periods up to 45 minutes at heat. Messrs.

Weldon and Bergen also have indicated that arc melted steel has a slightly finer grain than that melted in induction furnaces when treated under identical conditions. Mr. Gill on the contrary reports no practical difference in grain sizes of the several different brands of this steel examined by him. The author investigated several different brands in six different sizes, and found no practical difference due to manufacturing processes. Surely there is an explanation for these observed differences. It is the author's sincere hope that both steel and tool manufacturers may conduct a more extensive research to determine whether or not differences do exist and if they do, the reason for their existence. This is in line with Mr. Wyzalek's suggestion that elaboration of the test would be of practical use.

Moreover, the author would like to raise the question of what constitutes a fine- and coarse-grained steel. Is a steel which shows a grain count of 10.4 grains, according to the intercept method, materially different from one which shows a grain count of 11.6? Where shall we draw the line of demarcation between coarse- and fine-grained steel? Are there any tool manufacturers who know whether a steel showing a grain count of 12 is more or less efficient than a steel showing a grain count of 14? Will the type of tool have an influence upon the desired grain size? Snyder and Graeff have established a quantitative measure of grain size evaluation, which in the author's opinion is better than anything thus far devised. It is far superior to the old method of describing the grain size as coarse, fine, or some other nondescriptive term. However, this method of grain size determination is not infallible and judgment must be exercised in using it. It is possible that three inexperienced observers when examining the same microspecimen will report different results. Therefore, in discussing grain size, let us not be too critical of the results which we have at the present time, but rather endeavor to co-operate in an attempt to determine why these observed differences exist, and to correlate grain size with tool efficiency.

Messrs. MacLaren and Gill have observed differences in grain size which they attribute to the composition of the furnace atmosphere. The results obtained by the author do not show any material difference due to this variable. Also the specimens which were treated by the co-operative firms did not show any material difference as a result of different furnace atmospheres. The author agrees with Mr. Gill that the use of air, pure CO and CO_2 would have shown the extreme effects of atmospheres upon grain size. However, when this work was undertaken, the primary purpose was to determine the effects of atmospheres as found in commercial heat treating furnaces rather than to make an academic study of the effects of artificial atmospheres. In addition, Mr. Gill expressed his regrets that samples had not been treated from salt baths as compared to those treated from furnaces. The author has done this, but did not include the salt bath results since the primary purpose of the paper was to determine the effects of treating this type steel from furnaces only. The results which we obtained when treating from salt baths do not agree with those shown by Mr. Gill. Six sets of samples were treated by different concerns who employed salt baths for heat treating, and all of the results of the grain size determination, except one set, agreed with those treated from furnaces. Mr. Gill, no doubt, will agree that one of the most difficult problems in the use of

high temperature treatments is an accurate measurement of temperature and therefore some of the discrepancies which exist can be attributed to these errors.

The author thoroughly agrees with Mr. MacLaren that reducing atmospheres should be used for the heat treatment of a large majority of tools made from this type steel. The atmosphere range which Mr. MacLaren has found satisfactory is the one that the author usually recommends. It would be impractical to use oxidizing atmospheres because of the design of the tool.

Messrs. d'Arcambal and Gill are of the opinion that longer soaking times would be harmful rather than beneficial. When the author suggested that studies be made regarding the effects of time at heat, he did not have in mind the holding of the tools for hours at the hardening temperature, but rather to increase the time from zero to three or four minutes at heat. It is the author's opinion that many tools are not at the hardening temperature when quenched if the temperature is judged by the unaided eye. This is based on experience which indicates that judging temperatures at these high heats is very difficult. Moreover, Messrs. Weldon and Bergen have shown that a steel having the same grain count may have an entirely different martensitic structure. Whether this difference in structure is harmful or beneficial must be determined.

Mr. Gill's remarks concerning the effect of the segregate on grain size and fracture characteristics are appreciated. The author fully recognizes the effect that this variable has upon both the grain size and fracture characteristics of this steel, but deliberately eliminated the effects of segregation, as they are so well known. The author had hoped by giving very minute details under each particular test to preclude the discussion of the effect of segregation.

Messrs. Morrison and Gill have advanced the theory that the carburization which occurs during heat treating is due to the formation of CO or the deposit of a soot. The author also contemplated using the same theory when the paper was written, but the one proposed appears to be the more logical of the two. Another theory has been advanced to the effect that the carbide on the surface of the steel is slightly changed due to the partial oxidation and assumes a different molecular composition than it originally had. Because of this change in molecular composition, it is soluble in the matrix, even though the matrix is already saturated with the original carbide. Whatever the mechanics of the carburization, it is undoubtedly agreed that the carbon must be dissolved, and that it cannot migrate as granules of carbide. Before closing the discussion of the theory of carburization, the author would suggest that a sample of this steel be treated in a salt bath using salts which do not contain any carbon, but which have a slight washing action such as a mixture of boric acid and borax. Carbon analyses should be made before and after, and these results undoubtedly will throw some light upon the mechanism of carburization.

Regarding the observations which Mr. Morrison made concerning surface contact, the author agrees that decarburization or carburization may take place on the surface in contact with various materials. The author has found that either of these conditions may result when contact is made with carborundum, magnesium oxide, chrome oxide, or stainless steel trays. This condition has been attributed by the author, not to the material with which the steel makes contact, but rather to the stagnation of the amosphere. Whether decarburization or carburization takes place, is dependent upon the type of furnace atmosphere

employed. As further proof that these reactions are not related to the material contacting the steel, it is possible to take two machined surfaces of the same steel, and produce either of these conditions.

Mr. Tour's comments on the carburization of molybdenum high speed steel are interesting. The author agrees with Mr. Tour that the structure caused by carburization may be misinterpreted as decarburization, and in order to be able to distinguish between the two, considerable experience is necessary.

Mr. George apparently has misinterpreted some of the results given in the paper. The author did not have in mind that any atmosphere, regardless of its composition, would be satisfactory for the treating of high speed steel, as Mr. George has inferred. The author has little fear that the average hardener will be misled by the data given in the paper, since any high speed tool hardener knows that oxidizing atmospheres are very undesirable, and one of the primary purposes for the development of controlled atmospheres was to eliminate the detrimental effects caused by this type of atmosphere. Further, in Part I, Section 13, of the paper, the author very definitely states his position regarding the use of atmospheres containing free oxygen. To quote, "The surfaces obtained in oxidizing atmospheres in the author's opinion are definitely unsatisfactory for the treating of the majority of tools made from this type of steel. In addition to the large amount of scale, oxidizing atmospheres always produce a rough surface, frequently cause pitting, and often show the condition commonly referred to as 'alligator skin'. Oxidizing atmospheres further cause sharp corners or edges to become round due to scaling".

Mr. George further assumed that the author inferred that the carburization which normally takes place has a damaging effect. The author made no statement concerning either beneficial or harmful effects regarding this carburizing action. Mr. d'Arcambal in his discussion gave a specific case where this carburizing action apparently was beneficial. Since this subject has been brought forward, the author will express his opinion that this carburization will be beneficial only if the tools in question require wear resisting properties. On the other hand, if the tools are subject to impacts or shocks, this carburization would be definitely harmful. Moreover it is the author's opinion that this carburizing action has been taking place ever since 18-4-1 high speed steel has been in use. Furthermore, the large majority of tools are ground after heat treating, thereby removing the question as to whether or not carburization is harmful or beneficial. The greatest benefit to be derived from this carburization is the satisfaction of knowing that during normal heat treatment the tools are not decarburized, as decarburization has a more detrimental effect than a slight amount of carburization. Mr. George also has indicated that the degree of carburization may be controlled by changing the furnace atmospheres. To the contrary, the author has found that the degree or the amount of carburization cannot be controlled by regulating the furnace atmosphere. The author is of the opinion that if Mr. George would repeat the same experiments as indicated in his data, different results would be obtained.

KINETICS AND REACTION PRODUCTS OF THE ISO-
THERMAL TRANSFORMATION OF A 6 PER CENT
TUNGSTEN-6 PER CENT MOLYBDENUM
HIGH SPEED STEEL

By John L. Ham, Robert M. Parke and Alvin J. Herzig

Abstract

The S-curve of a 6 per cent tungsten-6 per cent molybdenum high speed steel was determined by dila-tometric, hardness and metallographic tests. The practical significance of the results is discussed briefly.

Introduction

THE pioneer work of Davenport and Bain (1),[1] which offered the first sound and quantitative explanation of the behavior of steel under nonequilibrium conditions, has opened to the metallurgist a field of research which promises to eliminate a great deal of uncertainty as to the response of various types of steel to hardening and other heat treating processes. Essentially the same technique used by Davenport and Bain in determining the familiar "S-curves" for plain carbon steels is applicable to the study of both high and low alloy steels. The curves obtained may, however, bear little or no resemblance to those for carbon steels, especially if elements such as tungsten or molybdenum are present in large amounts. These elements greatly retard the rate of transformation in the high temperature regions, and thus enable maximum hardness to be obtained by relatively slow cooling rates.

Such reaction-rate curves will, of course, predict exactly what will occur only in the case of light sections which are quenched rapidly from the austenitic state and isothermally treated. The curves can be applied to heavy sections only if the quench-cooling rate of each part of the section is known. For obtaining information which is fundamentally characteristic of the chemical composition of a steel and independent of mass, the determination of the S-curve by austempering experiments with small specimens is imperative. Thus,

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[1] The figures appearing in parentheses refer to the bibliography appended to this paper.

austempering experiments undoubtedly constitute one of the most valuable methods for determining the fundamental nature of the reactions occurring in a given steel during a specific heat treatment.

It is also believed that information gained by this method should be valuable in determining the procedure most likely to minimize the occurrence of internal stresses and cracks in intricate tools during the hardening process. Thus, in the case of high speed steel, it is known that interrupting the quench in the neighborhood of 1000 degrees Fahr. (538 degrees Cent.) by quenching in molten lead reduces the tendency toward cracking due to internal cooling stresses without appreciably affecting the final hardness or toughness of the steel (2). A knowledge of the rates of transformation may, therefore, reveal some range of temperature through which the steel might be slowly cooled after the lead quench, without transforming. Slow cooling throughout this region might reasonably be expected to reduce internal cracking to a minimum without adversely affecting the other qualities of the steel.

The particular steel under observation has been described elsewhere (3), (4) and was selected as one of the most promising types of molybdenum high speed steels developed in recent years. The range of chemical composition is as follows:

	Per Cent
Carbon	0.78 - 0.83
Manganese	0.20 - 0.40
Silicon	0.15 - 0.30
Chromium	3.75 - 4.25
Tungsten	5.75 - 6.25
Vanadium	1.40 - 1.60
Molybdenum	5.75 - 6.25

This steel anneals to about 228 Brinell, can be readily machined in this condition, and hardens to 65-67 Rockwell C when oil-quenched from 2275 degrees Fahr. (1246 degrees Cent.) and tempered at 1050 degrees Fahr. (566 degrees Cent.).

Although the heat treatment described above results in satisfactory performance of the steel, a determination of the S-curve promised to contribute much toward a better understanding of the nature of the hardening process. Accordingly, the various methods of determining the isothermal reaction rates were considered and those used in the original work of Davenport and Bain (1)—namely, dilatometric analysis, metallographic examination and hardness determinations, were selected as the most reliable methods available.

The remainder of this paper will be devoted principally to a description of the experiments performed to establish the S-curve for this particular steel and to the presentation and discussion of the results obtained.

PREPARATION OF SPECIMENS

The specimens were cut from hot-rolled and annealed bars of a commercial heat of the following analysis:

	Per Cent
Carbon	0.80
Manganese	0.23
Silicon	0.27
Chromium	4.07
Tungsten	5.70
Vanadium	1.65
Molybdenum	6.09

Preliminary tests were made to determine the length of time required at 2275 degrees Fahr. (1245 degrees Cent.) to dissolve most of the carbides without causing excessive grain growth or the formation of an eutectic at grain boundaries.

This steel has a lower critical point on heating at 1540 degrees Fahr. (840 degrees Cent.) and an upper critical on heating at 1610 degrees Fahr. (875 degrees Cent.) according to dilatometric tests.

AUSTEMPERING OF SPECIMENS FOR METALLOGRAPHIC EXAMINATION AND HARDNESS TESTS

All heat treatments were carried out in furnaces and quenching baths controlled to ± 5 degrees Fahr. by throttling type controllers. Lead baths were well deoxidized with charcoal while in use.

The specimens were preheated in a lead bath at 1500 degrees Fahr. (815 degrees Cent.) and placed in a tube furnace at 2275 degrees Fahr. (1245 degrees Cent.). They were then quenched in lead, oil or water to the particular subcritical temperature being investigated. After holding at constant temperature for the desired length of time, the specimens were water-quenched to room temperature, and the C scale Rockwell hardness determined. They were then mounted in bakelite, polished, etched in 10 per cent nital, and examined metallographically.

At the higher temperatures, when austempering for more than 10,000 seconds, the specimens were removed from the lead immediately after reaching the subcritical temperature of the bath and placed in a tube furnace which was then either evacuated or filled with nitrogen. Comparative tests in nitrogen and in a vacuum indicated that the presence of the nitrogen had no appreciable effect on the microstructure or hardness of the specimens. Whenever temperature and time conditions were such as to cause danger of decarburization, additional specimens of the same size and shape were treated along with the regular test specimens and subsequently analyzed for carbon. It was found possible to austemper in well-deoxidized lead up to 1530 degrees Fahr. (830 degrees Cent.) for 10,000 seconds without decarburization.

AUSTEMPERING OF SPECIMENS FOR DILATOMETRIC MEASUREMENTS

Two dilatometers of quite different design were used in this work. One of these was stationary, the specimen being maintained at the subcritical temperature by a vertical split tube furnace, while the other was a portable quenching dilatometer and measured the length of the specimen while immersed in a bath of lead alloy, oil or water. The stationary outfit was most suitable for the work at high temperatures—over 700 degrees Fahr. (370 degrees Cent.)—since in this region plenty of time was available, before the reaction started, to transfer the specimen to the dilatometer after quenching to the reaction temperature. At some of the lower temperatures, however, the reactions started almost immediately after the quench. The portable instrument was, therefore, designed so that the specimen could be inserted immediately upon removing it from the high temperature furnace. Changes in length of the specimen during cooling, as well as after reaching the temperature of the bath, could therefore be measured.

When the transformations were rapid, a dictaphone was used to co-ordinate the readings with time.

For investigation of transformation rates at 700 degrees Fahr. (370 degrees Cent.) and above, the specimens were preheated at 1500 degrees Fahr. (815 degrees Cent.) in lead, placed in the tube furnace at 2275 degrees Fahr. (1245 degrees Cent.), quenched in a lead bath to the subcritical temperature desired, and quickly placed in the stationary dilatometer furnace. This furnace was controlled at the

same temperature as the quenching bath, and was held at this temperature during the 11-day period over which observations were made. The specimens were finally water-quenched, examined metallographically, and tested for hardness in order to confirm the results obtained using the smaller metallographic specimens.

Below 700 degrees Fahr. (370 degrees Cent.) the same preheating and solution treatments were used, but the specimens were inserted in the portable dilatometer directly from the 2275 degrees Fahr. (1245 degrees Cent.) solution temperature and immediately
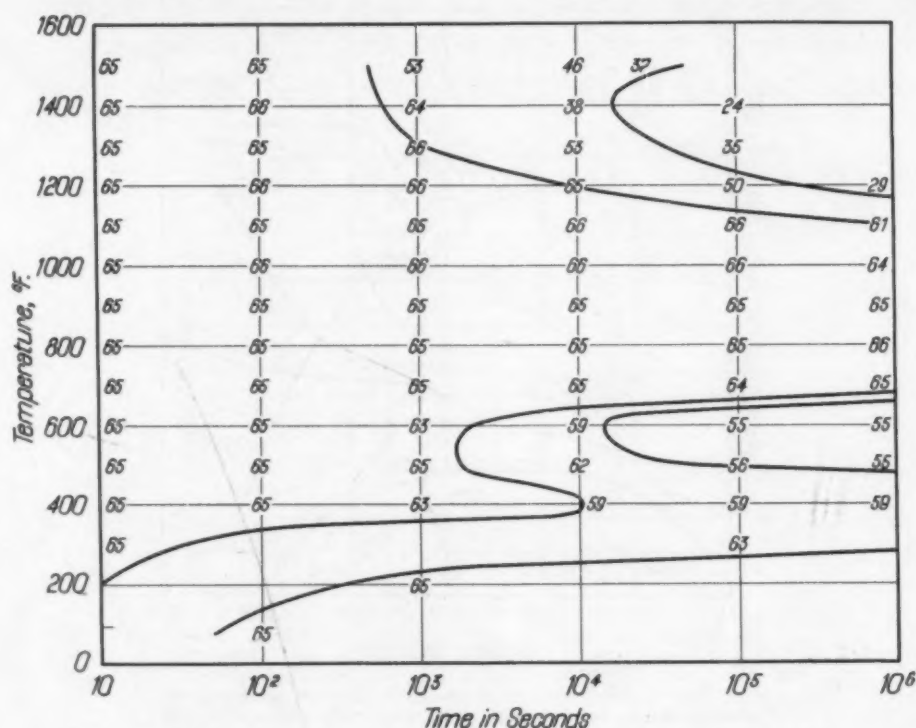
Fig. 1—S-Curve of Six Per Cent Tungsten—Six Per Cent Molybdenum High Speed Steel.

quenched in a pot of lead-bismuth, oil or water at the desired temperature. Readings were recorded by the dictaphone during the rapid contraction and periodically thereafter until the expansion due to transformation was complete.

INTERPRETATION OF RESULTS

Fig. 1 shows the isothermal behavior of this steel from room temperature to 1500 degrees Fahr. (815 degrees Cent.). The curves show the starting and finishing times of the reaction as determined by metallographic and hardness tests at intervals of 100 degrees

Fahr. and by dilatometer tests at greater or smaller intervals depending on the complexity of the curve in the particular range of temperature being investigated. Although the metallographic approach proved to be very useful in detecting the first traces of transformation, the curves were based principally on dilatometric results since these present a quantitative picture of the extent of the transformation at all times during the reaction, whereas the metallographic observations and hardness tests merely restrict the curve to certain time
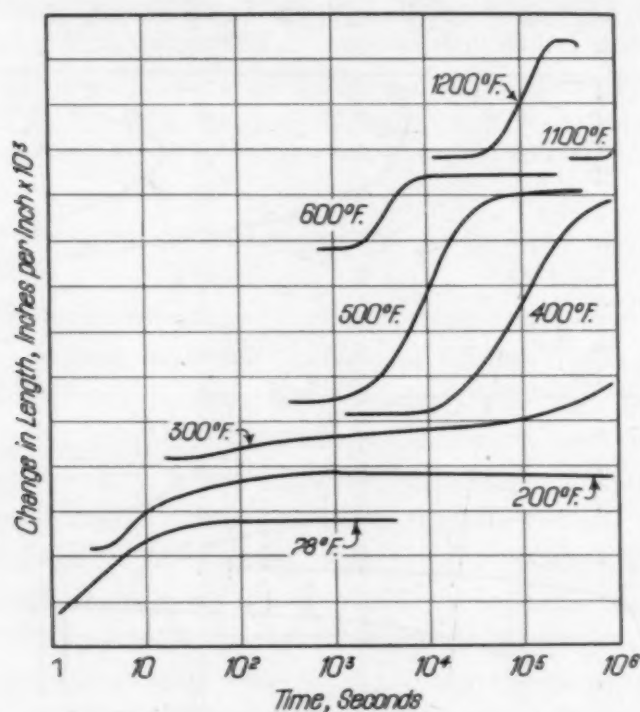
Fig. 2—Dilation Versus Time Curves at Constant Temperatures of 78, 200, 300, 400, 500, 600, 1100 and 1200 Degrees Fahr.

intervals and permit a semiquantitative estimate of the extent of the reaction at a limited number of points. Since the metallographic and hardness tests are necessarily indirect indications of the progress of transformation, they were used principally to determine the nature of the reaction products and to confirm the dilatometric results. The dilatometric test has the important advantage of permitting direct observations during transformation. Metallographic and hardness tests were made in general at elapsed times of 10, 100, 1000, 10,000, 100,000 and 1,000,000 seconds. Time was measured from the instant the specimens first assumed a constant length on cooling to the temperature of the quenching medium.

The numbers on Fig. 1 represent Rockwell C hardness values determined at room temperature after holding at the indicated temperature and for the time designated.

Dilation versus time curves at selected temperatures are shown in Fig. 2. The "S" shape is characteristic of most of the curves obtained.

It is felt that the meaning of the term "end-point" as used in this discussion should be clearly defined in order to avoid confusion with certain other work of this type. The end-point of the reaction at a given temperature has been taken as the time at which no further change in length occurs. Obviously this does not mean necessarily that all the austenite has transformed since, if the temperature is
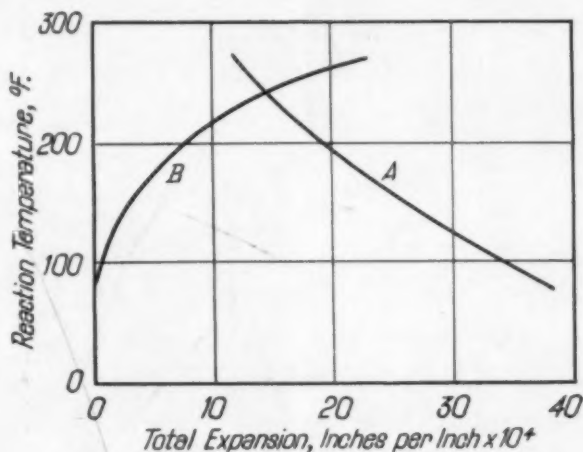
Fig. 3—Curve A, Total Isothermal Expansion Versus Reaction Temperature. Curve B, Expansion Obtained from Additional Austenite Conversion Versus Reaction Temperature. The Additional Austenite Transforms During Cooling from the Isothermal Reaction Temperature to Room Temperature, and During Reheating to the Reaction Temperature.

changed, further expansion may, and usually does, occur. It is evident from the curves of Fig. 2 that the total expansion varies greatly with the temperature. In this particular steel maximum expansion during 1,000,000 seconds occurred at 400 degrees Fahr. (205 degrees Cent.).

It is possible that, after reaching constant length at some particular temperature, the amount of untransformed austenite could be determined by quenching to room temperature or to some lower temperature at which all of the austenite transforms, reheating to the original reaction temperature, and noting the amount of expansion obtained. For practical purposes, however (such as the measure-

ment of hardenability) it is believed that a knowledge of the starting and finishing points of the reaction as it occurs at a given temperature, regardless of the degree of equilibrium attained when the reaction stops, is of primary importance. In the present case it is quite certain that at all temperatures from 78 to 600 degrees Fahr. (25 to 315 degrees Cent.) appreciable amounts of austenite are retained after the isothermal expansion has stopped, since additional expansion was invariably obtained by cooling to room temperature and reheating. From 300 to 78 degrees Fahr. (150 to 25 degrees Cent.) the isothermal expansion became continually greater, indicating that complete transformation of the austenite probably requires quenching to some temperature below 78 degrees Fahr. (25 degrees Cent.).

Total isothermal expansion in this range is shown in Curve A of Fig. 3 as a function of the temperature. Curve B (Fig. 3) shows the additional expansion obtained in each case by cooling to room temperature and reheating.

General Description of the S-Curve

The S-curve (Fig. 1) has a number of unusual characteristics. It is to be noted that the product of transformation between 1500 and 1100 degrees Fahr. (816 and 593 degrees Cent.) forms first at the grain boundaries (Fig. 4) and consists of minute dark-etching spheroids. This product is shown in Figs. 5 and 6 at more advanced stages. From 1000 to 700 degrees Fahr. (538 to 371 degrees Cent.) the austenite is apparently perfectly stable up to 1,000,000 seconds (about 11½ days). No evidence of any kind could be found to indicate any reaction in this region, consequently the nature of the product of transformation between 700 and 1000 degrees Fahr. (370 and 540 degrees Cent.) is unknown.

Another unusual feature is the apparent stability of the austenite at 400 degrees Fahr. (205 degrees Cent.). At this temperature the starting point of the reaction is considerably later than at 300 or 500 degrees Fahr. (150 or 260 degrees Cent.).

The reactions at 300 and 400 degrees Fahr. (150 and 205 degrees Cent.) show no definite end-points up to 1,000,000 seconds, whereas those at 500 and 600 degrees Fahr. (260 and 315 degrees Cent.) exhibit definite end-points at 75,000 and 14,500 seconds respectively.

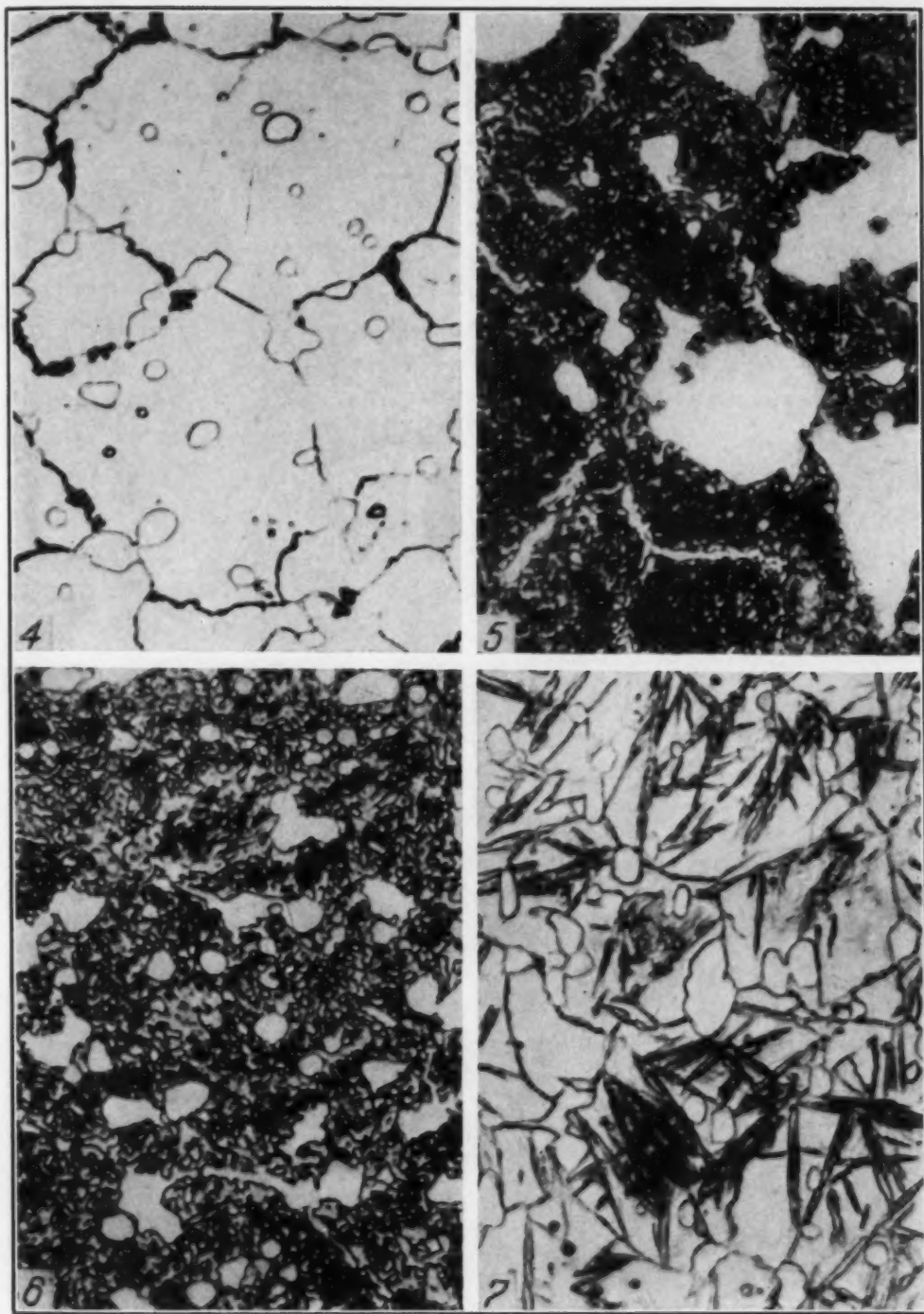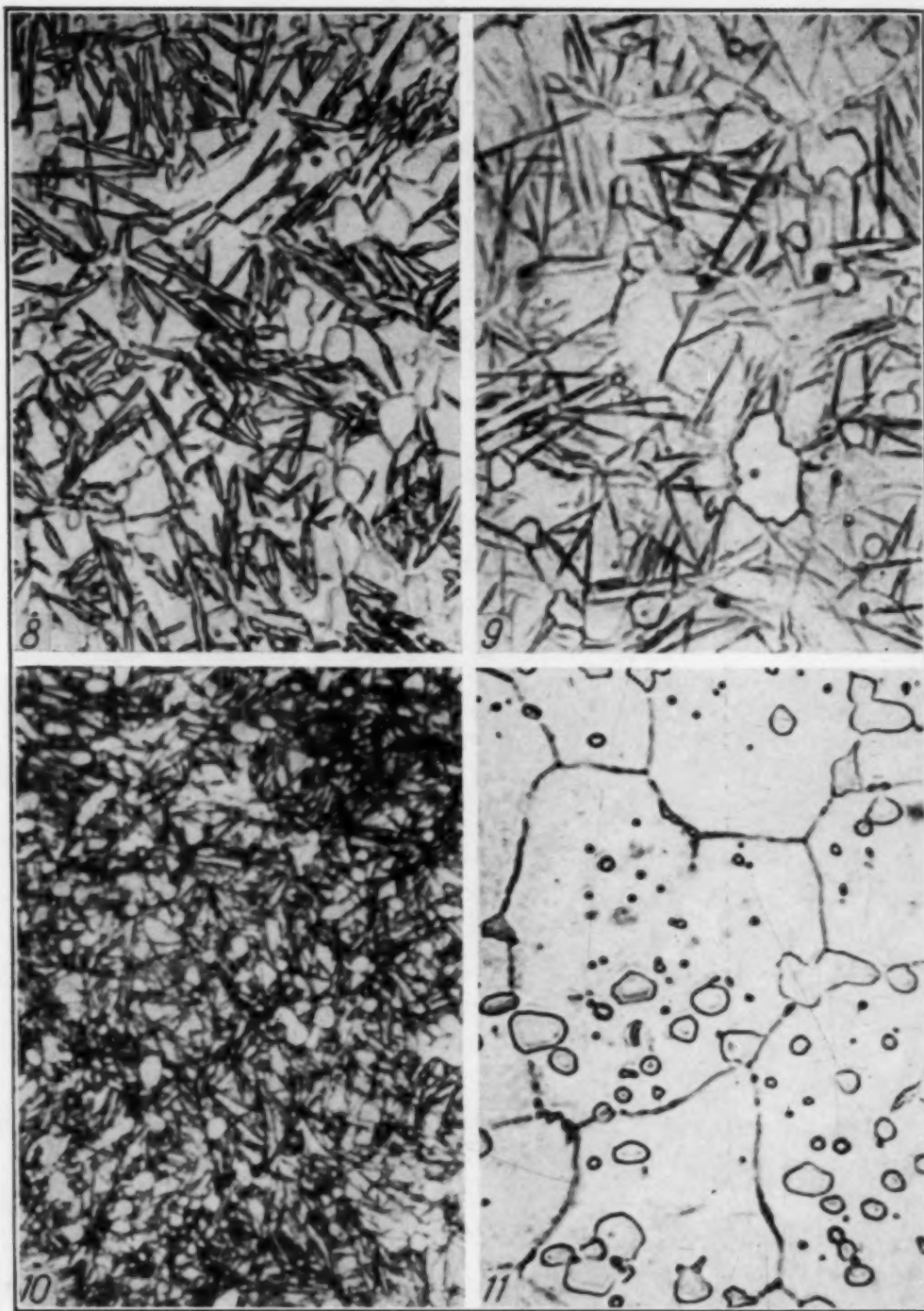At 600 degrees Fahr. (315 degrees Cent.) and below, the product

Fig. 4—Structure Obtained by Isothermal Reaction for 1000 Seconds at 1400 Degrees Fahr. Etched in 10 Per Cent Nital. × 1500.

Fig. 5—Structure Obtained by Isothermal Reaction for 10,000 Seconds at 1400 Degrees Fahr. Etched in 10 Per Cent Nital. × 1500.

Fig. 6—Structure Obtained by Isothermal Reaction for 100,000 Seconds at 1400 Degrees Fahr. Etched in 10 Per Cent Nital. × 1500.

Fig. 7—Structure Obtained by Isothermal Reaction for 10,000 Seconds at 600 Degrees Fahr. Etched in 10 Per Cent Nital. × 1500.

Fig. 8—Structure Obtained by Isothermal Reaction for 1,000,000 Seconds at 600 Degrees Fahr. Etched in 10 Per Cent Nital. ✕ 1500.
Fig. 9—Structure Obtained by Isothermal Reaction for 10,000 Seconds at 500 Degrees Fahr. Etched in 10 Per Cent Nital. ✕ 1500.
Fig. 10—Structure Obtained by Isothermal Reaction for 1,000,000 Seconds at 500 Degrees Fahr. Etched in 10 Per Cent Nital. ✕ 1500.
Fig. 11—Structure Obtained by Isothermal Reaction for 1,000,000 Seconds at 900 Degrees Fahr. Etched in 10 Per Cent Nital. ✕ 1500.

of isothermal transformation is acicular as shown in Figs. 7, 8, 9, 10. A lamellar structure does not occur in this steel unless it be produced by holding for very long times in the range 700 to 1000 degrees Fahr. (370 to 540 degrees Cent.).

The structure obtained after holding 1,000,000 seconds at 900 degrees Fahr. (480 degrees Cent.), which is practically identical to that obtained by a direct water quench from 2275 degrees Fahr. (1245 degrees Cent.), is shown in Fig 11.

Below 400 degrees Fahr. (204 degrees Cent.) the time for initiation and virtual completion becomes rapidly shorter. But even at room temperature some 50 seconds elapse before the transformation of austenite has reached the degree of completion attained at any time up to 11½ days.

It is of interest to note that the behavior of this steel as shown by the S-curve of Fig. 1 is similar to that of the 18-4-1 type (18 per cent tungsten, 4 per cent chromium, 1 per cent vanadium) as described by Cohen and Koh (5) in that little or no transformation of austenite occurs at the usual drawing temperature of 1050 degrees Fahr. (566 degrees Cent.).

SIGNIFICANCE OF THE RESULTS

It has already been suggested that internal stresses and cracking might be reduced by interrupting the quench and cooling slowly throughout the range of temperatures in which the austenite is stable for reasonably long periods of time. It appears from the S-curve (Fig. 1) that the quench could be interrupted for a short time at a temperature as high as 1100 degrees Fahr. (595 degrees Cent.) and the steel slowly cooled down to 400 degrees Fahr. (205 degrees Cent.) before quenching to room temperature. No reduction of the final hardness or toughness of the steel should result from such a treatment. This treatment may be useful in hardening intricate shapes or tools with plain carbon or low alloy steel shanks.

Considering the comparatively low temperature at which this steel must transform during an oil quench, it is remarkable that cracking is not encountered frequently, even in simple shapes. The obvious explanation of this phenomenon is that sufficient austenite is retained even at room temperature to accommodate the volume changes during transformation.

The S-curve clearly indicates the necessity of cooling this steel

to room temperature before drawing at 1050 degrees Fahr. (565 degrees Cent.). It is also evident that "direct drawing" by an interrupted quench at 1050 degrees Fahr. (566 degrees Cent.) will not produce the results of a conventional quench and draw.

SUMMARY

In the range 1500 to 78 degrees Fahr. (815 to 25 degrees Cent.) the S-curve of a 6 per cent tungsten—6 per cent molybdenum high speed steel has been determined by dilatometric, hardness and metallographic tests. The curve discloses that the austenite of this steel transforms very slowly, if at all, between 1100 and 700 degrees Fahr. (595 and 370 degrees Cent.) when quenched from a solution temperature just below the solidus. The rate of transformation is not rapid at any temperature between 1500 degrees Fahr. (815 degrees Cent.) and room temperature, but is faster at room temperature than at any other investigated. It would, therefore, be expected that this steel will undergo transformation close to room temperature when oil-quenched in light sections and consequently might be prone to develop quenching cracks. That such cracks do not occur frequently must be attributed to the retention of considerable amounts of austenite.

Between room temperature and 700 degrees Fahr. (370 degrees Cent.) the austenite of this steel is converted to an acicular product, while between 1100 and 1500 degrees Fahr. (595 and 815 degrees Cent.) the product is spheroidal.

On the basis of the information revealed by the S-curve, certain of the present methods of heat treating the steel are discussed.

Bibliography

1. E. S. Davenport and E. C. Bain, "Transformation of Austenite at Constant Subcritical Temperatures," *Transactions,* American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, p. 117.
2. M. A. Grossmann and E. C. Bain, "High Speed Steel," John Wiley & Sons, Inc., 1931, p. 142-144.
3. Experimental Report No. 359; Watertown Arsenal, Watertown, Mass., June 30, 1930.
4. Belgian Patent No. 434635—A. J. Herzig, Climax Molybdenum Co.
5. M. Cohen and P. K. Koh, "The Tempering of High Speed Steel," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 1015.

DISCUSSION

Written Discussion: By Miles K. Smith, chief metallurgist, Latrobe Electric Steel Co., Latrobe, Pa.

The authors are to be commended for their contribution to the knowledge of the transformation taking place in high speed steel during the various time temperature curves which they have so ably presented. I have often thought that our lack of knowledge of the processes involved in the heat treatment of high speed steel has in many instances hampered the ultimate life of tools made from this steel. It is only through papers such as this that a more thorough understanding of the processes of hardening so complex an alloy will ultimately lead to the maximum efficiency of steels of this type. By so improving our knowledge, we may eventually be able to explain the occasional tool which performs far in excess of normal tool life for a particular job and by all practical methods of metallurgical investigation, we can arrive at no definite explanation for its unusual performance. If, by increased knowledge of the better heat treatments of steels of this type, we can make this exceptional case the rule rather than the exception, we will have accomplished a gigantic step in the improvement of the performance of high speed steel tools.

Of particular note is the extremely high hardnesses obtained by holding the temperatures of 1000 to 1300 degrees Fahr. as shown in Fig. 1 time temperature curve. The structures corresponding to transformations taking place within this temperature range should be the dark-etching spheroidal shapes shown in Figs. 4, 5 and 6. I would like to inquire if the authors have any additional comments to make regarding its maintaining its high Rockwell hardness if drawn at temperatures in the vicinity of 1050 degrees Fahr. I would also like to hear further discussion on the length change taking place at 400 degrees Fahr. which corresponds to the maximum change of any of the temperatures studied, as shown in Fig. 2. The time required for this transformation to approach equilibrium at this temperature corresponds to 10^4 seconds with a comparatively low Rockwell hardness of C 59. The secondary hardness of this sample produced by a draw of 1050 degrees Fahr. may show a much higher Rockwell hardness. I would like to ask the authors if they have checked this possibility.

I would also like to emphasize the fact mentioned by the authors that steels of this type should be cooled to room temperature before drawing at 1050 degrees Fahr. Owing to the many intricate shapes of tools which are made from steels of this type, it is often not desirable to go quite as low as room temperature, particularly since this temperature may vary with weather conditions which might result in cracking of the tools during such a drastic treatment. However, I wish to emphasize that all tools should be cooled to a maximum of 200 degrees Fahr. and allowed to remain at this temperature for sufficient time to complete transformation before taking to the drawing temperature. In many instances, we have found incomplete quenching followed by a draw has not produced the desired structures, consequently causing tool failure.

We have recently made a study of the toughness of 6 per cent tungsten—

6 per cent molybdenum high speed steel, using various methods of heat treatment, among which was a delayed quench at 1000 degrees Fahr. followed by an air cool. The Rockwell hardness of this sample after being drawn at 1050 degrees Fahr. was 63. As pointed out by this paper, a delayed quench of 1000 degrees Fahr. over normal periods of time should show no transformation at this temperature, the sample continuing to be austenitic down to just under 400 degrees Fahr. By this method of quenching, we have found that the steel possesses additional toughness over that obtained by the normal quench and draw, as measured by a deflection sample ½ inch round supported at 6-inch centers. As this sample corresponded closely to the data shown in this paper, the toughness measurements were approximately 25 per cent higher by this method of quenching than were obtained by the conventional oil quench as measured by this deflection test.

Again let me congratulate the authors on this excellent piece of work and express my hope that they will see fit to continue this work by similar heat treatments followed by conventional draws at 1050 degrees Fahr. in order to establish the physical properties and cutting tests conducted on specimens hardened by these various treatments.

Written Discussion: By W. R. Breeler, assistant to vice president, Allegheny Ludlum Steel Corp., Dunkirk, N. Y.

The data presented by the authors of this paper is a timely contribution, because the type of steel studied is one of considerable commercial interest. In a paper delivered two years ago by the writer, attention was called to a balanced alloy containing approximately—

	Per Cent
Tungsten	5.25
Molybdenum	4.00
Vanadium	1.50
Chromium	4.00
Carbon	0.80

Although this analysis differs slightly from the one reported in the paper, it is believed to be sufficiently close for all practical purposes to present a few observations. In the summary of the paper, it is stated that the 6 per cent tungsten-6 per cent molybdenum steel might be prone to develop quenching cracks when oil quenched in light sections. It is also stated "that such cracks that do not occur frequently must be attributed to the retention of considerable amounts of austenite". Whether or not the same observation would hold for the 5.25 tungsten—4.00 molybdenum steel is not definitely known. However, the writer wishes to point out that after carefully observing the manufacture of a great many tons of the 5.25 tungsten—4.00 molybdenum steel, and following the manufacture of tools made therefrom, the latter composition is not unduly sensitive to cooling. In other words, for all practical purposes, this new cutting steel is quite foolproof in manufacturing as well as heat treatment.

Oral Discussion

I. E. WAECHTER:[1] I should like to ask the authors whether any difficulty is experienced with this high speed steel as far as decarburization is concerned,

[1]Materials and research engineer, City Street Railroad Commissioner's Office, Cleveland.

incident to heat treatment, as is known to be the case with the "Momax" type of molybdenum high speed steel of somewhat different composition.

Authors' Reply

The authors express their gratitude to Mr. Smith for his interesting discussion of their paper.

The ability of this steel to retain its hardness on drawing at 1050 degrees Fahr. must be due in part at least to an inherent structural stability of the martensite at this temperature. It has been shown by Cohen and Koh[2], for the 18-4-1 type of high speed steel, that secondary hardening is partly due to the precipitation of complex carbides from previously-retained austenite at the drawing temperature and partly to the transformation, at relatively low temperatures, of this residual austenite during cooling after the drawing operation. It is possible that the same explanation applies to the 6 per cent tungsten-6 per cent molybdenum type. It is probably true, as Mr. Smith suggests, that any transformation of austenite at 1050 degrees Fahr. would yield a relatively soft product.

With regard to the specimen held for 10,000 seconds at 400 degrees Fahr., it should be emphasized that this specimen had just barely started to transform when quenched to room temperature and therefore should react to drawing in about the same manner as a specimen quenched directly from 2275 degrees Fahr. to room temperature. It seems probable therefore that it *would* show a secondary hardening effect if drawn at 1050 degrees Fahr. No experiments have been performed to confirm this, however.

The results obtained by Mr. Smith by a delayed quench at 1000 degrees Fahr. followed by an air cool are very encouraging.

The authors wish to thank Mr. Smith for calling these results to their attention.

Mr. Breeler's discussion of this paper is very welcome. It is interesting to learn, from one who has been in intimate contact with the production and use of this type of steel, that it performs satisfactorily and is not unduly sensitive to cracking.

As to the decarburization tendency of this steel, it is safe to say that it is superior to the straight molybdenum type of high-speed steel.

[2]Morris Cohen and P. K. Koh, "The Tempering of High Speed Steel," TRANSACTIONS. American Society for Metals, Vol. 27, 1939, p. 1015-1047.

EFFECT OF RATE OF HEATING THROUGH THE TRANS-
FORMATION RANGE ON AUSTENITIC GRAIN SIZE

By Samuel J. Rosenberg and Thomas G. Digges

Abstract

Data are presented to show how the rate of heating through the transformation range affects the austenitic grain size at various temperatures of high-purity alloys of iron and carbon, and commercial and experimental plain carbon steels. The commercial steels included heats produced under furnace practice that resulted in both controlled and noncontrolled grain size. In certain cases, the austenitic grain size of these alloys and steels was affected by the rate of heating through the transformation range, but all the materials did not respond in the same manner.

Introduction

THE influence of austenitic grain size on many properties of steel has been widely discussed during the past decade and is now generally recognized. Not so much attention has been paid, however, to the study of factors which influence the austenitic grain size. Probably this has been due, at least in part, to the belief that a steel, once made, had what was termed an "inherent" grain size. The word "inherent" denotes unchanging, and its unfortunate use conveyed the idea to many that at any selected temperature a particular steel had a definite grain size and that this remained fixed regardless of other factors.

In a previous study of the influence of austenitic grain size on the hardenability of high purity iron-carbon alloys (1)[1] it was observed that the rate of heating through the transformation range often had a pronounced influence on the final austenitic grain size. If steels are similarly affected, this factor deserves consideration. This becomes especially important when consideration is given to the wide

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[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

range in heating rates commercially employed, varying from the extremely rapid heating secured in induction hardening to the slow rates obtained with furnace heating of large parts.

The present study was made to show the effect of the rate of heating to different temperatures on the austenitic grain size of high purity alloys of iron and carbon and of experimental and commercial plain carbon steels, with a wide range in carbon content. The commercial steels also differed in the method of deoxidization. The effects of other factors that influence the austenitic grain size, such as initial structure, amount of hot and cold working, time at maximum temperature, etc. were not investigated.

Previous Investigations

Excellent reviews of our knowledge concerning grain size have been given by Ward and Dorn (2) and by Shapiro (3). The review by Ward and Dorn in particular contains an extensive bibliography.

Although these reviews reveal a wealth of information relating to the effect of austenitic grain size upon the properties of steel, very few data, aside from the effect of furnace practice, are available to indicate the effect of other variables upon the grain size and these data are frequently contradictory. This is especially true with regard to the effect of the rate of heating.

Grossmann (4) found that different rates of heating had no effect upon the McQuaid-Ehn grain size of a 0.17 per cent carbon steel carburized at 1700 degrees Fahr. (925 degrees Cent.) for 2 hours. Three samples were tested. The time of heating from room temperature to carburizing temperature was approximately 2.5 hours, 30 minutes, and 5 minutes. All specimens had the same McQuaid-Ehn grain size (A.S.T.M. grain size No. 5).

Digges and Jordan (5), in their investigation of the hardening characteristics of 1 per cent carbon tool steels (having "controlled" and "noncontrolled" grain sizes) studied the effect of the rate of heating upon the austenitic grain size in an indirect manner. Their work was concerned primarily with the depth of hardening obtained in ¾-inch round specimens quenched from 1425 and 1550 degrees Fahr. (775 and 845 degrees Cent.). With all other factors constant, the depth of hardening was influenced by the grain size at the time of quenching, a coarser austenitic grain being reflected in greater

depth of hardening. Variations, from 1 to 13 minutes, in the time required for the center of the ¾-inch rounds to reach the hardening temperatures had no significant influence on the depth of hardening of the two steels.

The effect of the rate of heating upon the austenitic grain size of 0.80 per cent carbon steel was studied by Tobin and Kenyon (6). Specimens about 0.05 inch thick were heated at rates of 1.12 and 800 degrees Fahr. per minute through the interval of 1300 to 1400 degrees Fahr. (705 to 760 degrees Cent.), which included the critical temperature. They were then held at 1400 degrees Fahr. (760 degrees Cent.) for 1 hour, after which all of the specimens had an A.S.T.M. grain size No. 6. This procedure was repeated at 1500 degrees Fahr. All specimens again were found to have the same grain size, which in this case was designated by Tobin and Kenyon as No. 5½. "Thus," they concluded, "the austenitic grain size of this steel was independent of the investigated rates of heating through the critical."

Herty, McBride, and Hough (7) studied the effect of the rate of heating through the transformation range on the grain size of a silicon-killed 0.33 per cent carbon steel deoxidized with silicon and 0.41 per cent carbon steel deoxidized with aluminum. Half-inch cubes were heated at 1830 degrees Fahr. (1000 degrees Cent.) for 1 hour in order to produce a coarse-grained structure, air-cooled, and then heated through the transformation range at various rates to 1520 degrees Fahr. (825 degrees Cent.). The following data show the influence of heating rate upon the originally coarse-grained structure (3.3 grains per square inch at 100 diameters) of the "silicon-killed" steel.

Rate of heating—degrees Fahr. per min.	Grains/in² at x 100
2.0	368
4.0	164
5.6	25
8.5	7.6
11.0	8.4
12.6	6.4
18.0	6.0

When a ¼-inch cube of this steel in the coarse-grained condition was placed in the furnace at 1520 degrees Fahr. (825 degrees Cent.) and removed 5 minutes after it had come to the temperature of the

furnace, no grain refinement could be observed. The same experiments were made on the aluminum-treated steel, having initially a coarse-grained structure. At all heating rates an extremely fine grain was formed, about 200 grains per square inch at 100 diameters.

In the present report the term "grain size" will be used to denote the grain size of the austenite established at the maximum temperatures.

EQUIPMENT AND PROCEDURE

To insure adequate control of the rate of heating between extremely wide limits, it was necessary to use small specimens, approximately 0.1 inch square by about 0.04 inch thick. The specimens were heated in vacuo except when a lead bath was utilized to obtain maximum rates of heating. Specimens heated in vacuo were suspended from a 32-gage chromel-alumel thermocouple. One wire of the thermocouple was spot-welded to the center of the flat face of the specimen and the other wire was spot-welded to the center of the opposite face. The specimen was located within the heating chamber in the center of a chromel heating coil, $\frac{1}{4}$ inch in diameter by $\frac{1}{2}$ inch long. This heating chamber has been described in detail by Digges (1).

As a measure of the rate of heating, the time to heat from 1325 to 1450 degrees Fahr. (720 to 790 degrees Cent.) was used. This temperature interval included the Ac_1-Ac_3 points (1340 and 1425 degrees Fahr. respectively) in 0.50 per cent carbon steel, the material on which the first tests were made. In some of the high carbon alloys, the Ac_{cm} point occurred at a higher temperature than 1450 degrees Fahr. (790 degrees Cent.), but it was believed that the rate of heating through this point would not be significant in comparison with the rate through the Ac_{1-2-3} transformation.

In conducting the tests in vacuo, the specimens were heated rather rapidly to a temperature somewhat below 1325 degrees Fahr. (720 degrees Cent.) then at the desired rate through the range 1325 to 1450 degrees Fahr. (790 degrees Cent.), and then again rapidly to the required temperature. For the fastest rates of heating, specimens were plunged into a lead bath maintained at the desired temperature. With the small specimen used, an extremely rapid rate of heating (practically instantaneous) through the temperature range 1325 to 1450 degrees Fahr. was obtained in the lead bath. All specimens

were held at the maximum temperature for 15 minutes and then cooled in a manner suitable for outlining the austenitic grains with a proeutectoid constituent. The specimens were not all cooled alike from the temperatures establishing the austenitic grains. Variations, therefore, existed in the final structures produced in the specimens and, in some cases, the specimens were lightly repolished after etching to aid in the delineation of the parent austenitic grains.

After preparing the specimens for microscopic examination, grain counts were made by two observers, usually at four different locations. Grain counts were made in a circle, 7.75 square inches in area, and when possible were made at a magnification of 100 diam-

Table I
Grain Size Corresponding to American Society for Testing Materials Index Numbers

A.S.T.M. Grain Size Number	Number of Grains Per Square Inch at × 100	
	Minimum	Maximum
1	¾	1½
2	1½	3
3	3	6
4	6	12
5	12	24
6	24	48
7	48	96
8	96	192

eters. Fine-grained steels were counted at higher magnifications. Since actual grain counts on steels having a decidedly mixed grain size are meaningless, in these cases the relative amounts of the predominating grain sizes were estimated according to the grain-size classification of the American Society for Testing Materials, which is given in Table I.

In theory the delineation of austenitic grains is simple. A steel need only be heated to the required temperature and cooled so as to reject a proeutectoid constituent to the austenitic grain boundaries which, after suitable etching, are revealed by microscopic examination at room temperature.

This procedure, however, is somewhat difficult in the case of small specimens of hypoeutectoid steels. In order to outline the grains properly, the specimen must be cooled at exactly the right rate. Too fast a rate of cooling does not allow the precipitation of sufficient ferrite to definitely outline all the grains. A grain count on such a specimen is usually low, that is, the grains appear to be coarser than they actually are. Too slow a rate of cooling results in the precipitation of too much ferrite, accompanied by coalescence of

the ferrite and obliteration of the outline of the original austenitic grains. The result of a grain count on such a specimen usually is high, that is, the grains appear to be finer than they actually are.

With hypereutectoid steels, containing at least 1 per cent carbon, it is not difficult to outline the grains at temperatures sufficiently high to dissolve the cementite completely. At the lower temperatures used for hardening these steels, however, the excess cementite tends to spheroidize and on cooling is not precipitated solely at the boundaries of the parent austenite grains.

MATERIALS

High Purity Alloys of Iron and Carbon

The alloys used in this study were the same as those in previous investigations and their preparation has been described in a previous report (8). Essentially, the preparation consisted in carburizing hot- and cold-worked specimens of vacuum-melted electrolytic iron in a mixture of hydrogen and benzene vapor, and subsequently homogenizing by heating in vacuo at 1700 degrees Fahr. (925 degrees Cent.). Cooling from the temperature used in homogenizing was sufficiently rapid to produce sorbite (fine pearlite) in all the alloys. Specimens used for the determination of grain size had an initial structure of sorbite, as shown in Fig. 1.

Results of spectrochemical and chemical analyses and the determination of the gas content by the vacuum-fusion method showed that sulphur, nickel, cobalt and oxygen were the major impurities in the alloys. These elements amounted to about 0.021 per cent, whereas the total percentage (by weight) of all impurities determined was about 0.030. The compositions of the alloys are given in Table II.

Commercial Plain Carbon Steels

Commercial plain carbon steels containing approximately 0.5 and 1 per cent carbon were used. Two heats containing 0.5 per cent carbon were furnished through the courtesy of a large producer, and two heats of tool steel containing 1 per cent carbon were purchased through regular channels of supply. As shown in Table II, the most significant difference in the chemical compositions of the hypoeutectoid steels was in the content of aluminum and of aluminum
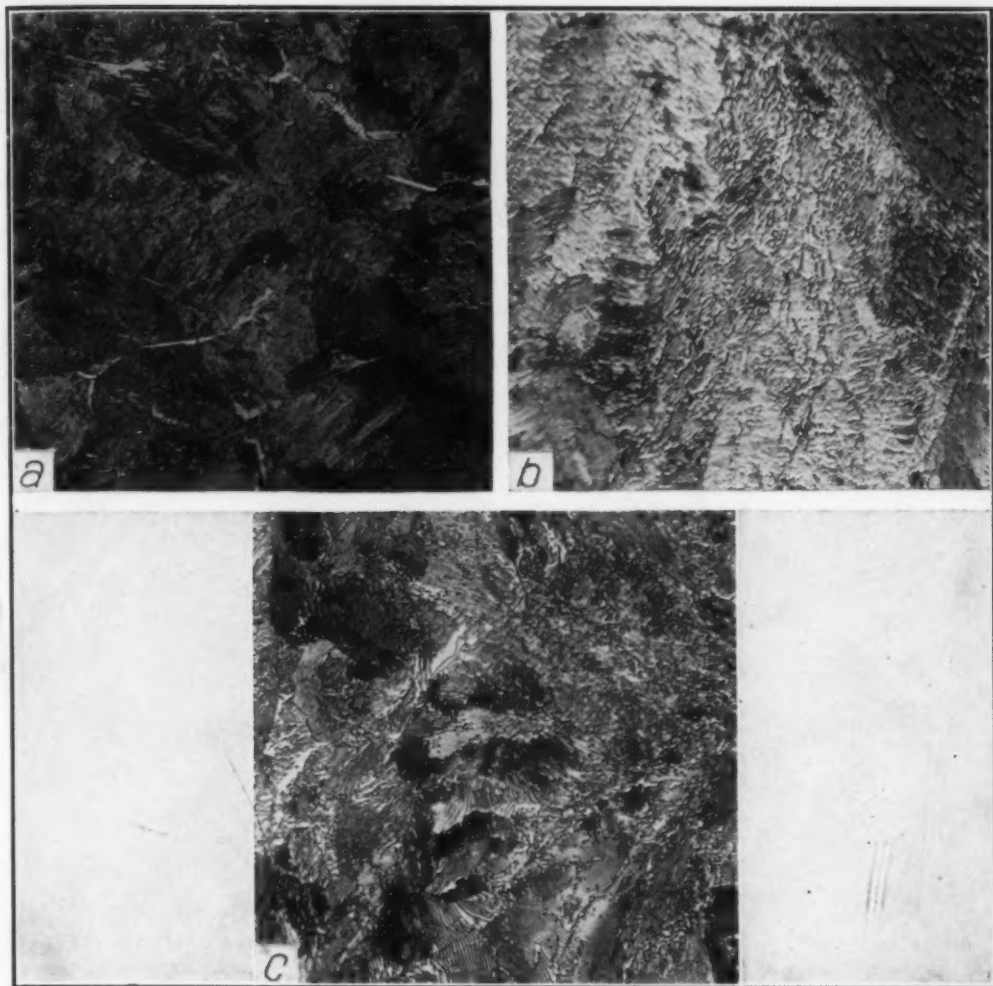
Table II
Chemical Composition of Materials Used

| Identification | Chemical Composition (Per Cent by Weight) | | | | | | | | | | | | | | | |
	C	Mn	P	S	Si	Cr	Ni	Co	Mo	V	Al₂O₃	Acid Soluble Al	Total Al	H₂	O₂	N₂
High Purity Alloys of Iron and Carbon																
HP-1	0.50	0.002	<0.001	0.004	0.002	.....	0.007	0.007	.....	.....	.....	.....	.....	0.0002	0.003	0.001
HP-2	1.01	0.002	<0.001	0.004	0.002	.....	0.007	0.007	.....	.....	.....	.....	.....	0.0002	0.003	0.001
HP-3	1.21	0.002	<0.001	0.004	0.002	.....	0.007	0.007	.....	.....	.....	.....	.....	0.0002	0.003	0.001
Commercial Steels																
C-1	0.49	0.79	0.023	0.023	0.22	.....	.....	.....	.....	.....	0.001	0.002	0.0025	0.0002	0.004	0.004
C-2	0.49	0.80	0.022	0.028	0.21	.....	.....	.....	.....	.....	0.007	0.016	0.0195	0.0002	0.003	0.004
C-3	1.05	0.28	0.019	0.013	0.22	0.08	0.13	.....	<0.01	<0.01	0.006	0.001	0.004	0.0002	0.007	0.009
C-4	1.06	0.26	0.013	0.011	0.19	0.09	0.10	.....	<0.01	<0.01	0.010	0.008	0.013	0.0003	0.009	0.007
Experimental Steels (Pack Carburized)																
PC-1	0.48	0.46	0.043	0.025	0.15	0.02	0.011	.....	.....	Trace	0.017	0.006	0.015	.....	.....	.....
PC-2	1.12	0.46	0.043	0.025	0.15	0.02	0.011	.....	.....	Trace	0.017	0.006	0.015	.....	.....	.....
Experimental Steels (Gas Garburized)																
GC-1	0.57	0.46	0.043	0.025	0.15	0.02	0.011	.....	.....	Trace	0.017	0.006	0.015	.....	.....	.....
GC-2	1.02	0.46	0.043	0.025	0.15	0.02	0.011	.....	.....	Trace	0.017	0.006	0.015	.....	.....	.....

Fig. 1—Initial Structure of Iron-Carbon Alloys. (a) 0.50 Per Cent Carbon (HP-1). × 100. (b) 1.01 Per Cent Carbon (HP-2). × 500. (c) 1.21 Per Cent Carbon (HP-3). × 500. Etched with 1 Per Cent Nital.

oxide. Similarly, the hypereutectoid steels differed in the proportions of aluminum and aluminum oxide. The heats containing appreciably higher proportions of metallic aluminum (that soluble in acid) and aluminum oxide were produced under conditions intended to control the austenitic grain size; the heats of relatively low total aluminum content were produced under conditions which resulted in noncontrol of austenitic grain size. All heats were representative of good commercial open-hearth practice. For the determination of grain size, specimens of the hypoeutectoid steels were used in the hot-rolled condition with an initial structure of sorbite and ferrite (Figs. 2a and b). The hypereutectoid steels were annealed to produce an initial structure of spheroidized cementite (Figs. 2c and d).
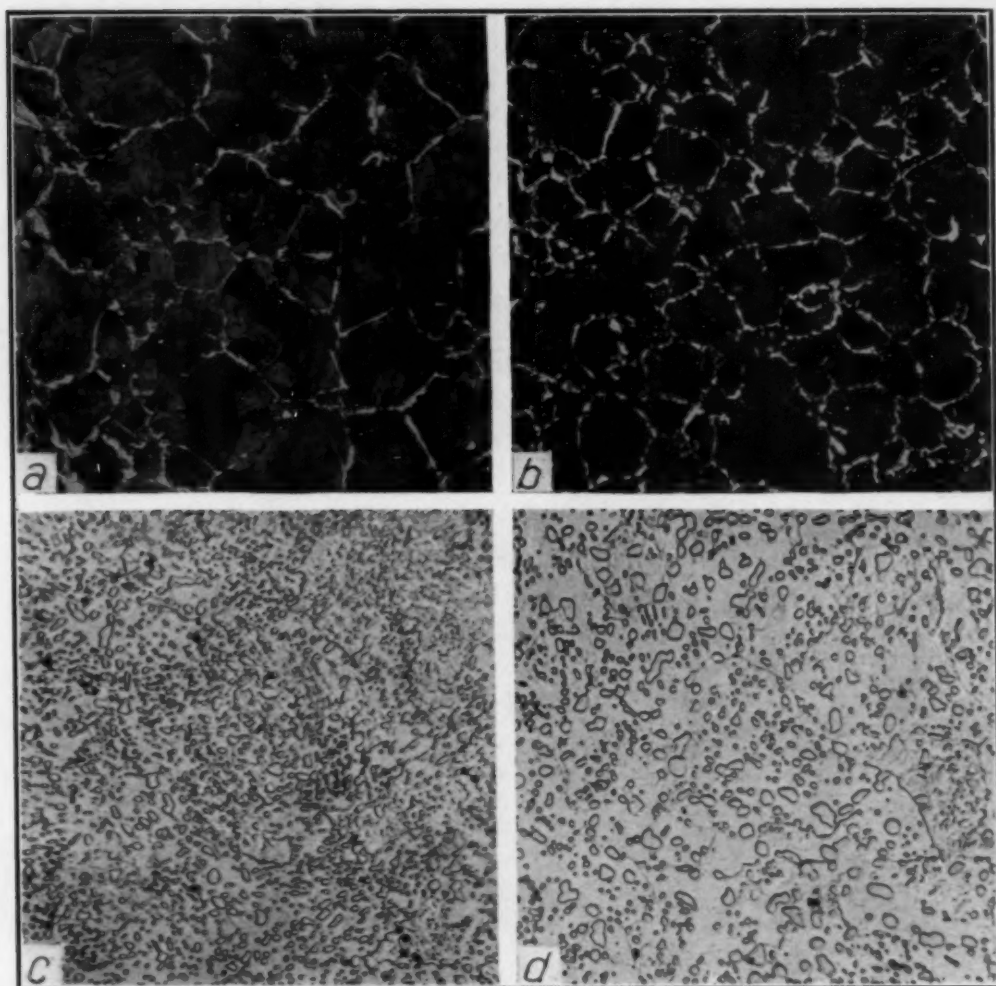
Fig. 2—Initial Structure of Commercial Plain Carbon Steels. (a) 0.49 Per Cent Carbon (C-1). × 100. (b) 0.49 Per Cent Carbon (C-2). × 100. (c) 1.05 Per Cent Carbon (C-3). × 500. (d) 1.06 Per Cent Carbon (C-4). × 500. Etched with 1 Per Cent Nital.

Experimental Plain Carbon Steels

Two series of carbon steels were prepared from specimens cut from a forging of a plain carbon steel, which contained 0.20 per cent carbon and appreciable amounts of aluminum. The first series was prepared by pack-carburizing these specimens in a mixture of approximately 85 per cent wood charcoal and 15 per cent barium carbonate at 1700 degrees Fahr. (925 degrees Cent.) for various periods of time. The carburized specimens were homogenized by pack annealing at 1700 degrees Fahr. for 4 to 5 hours before normalizing from the usually recommended temperature range. The second series was prepared by carburizing specimens in hydrogen-
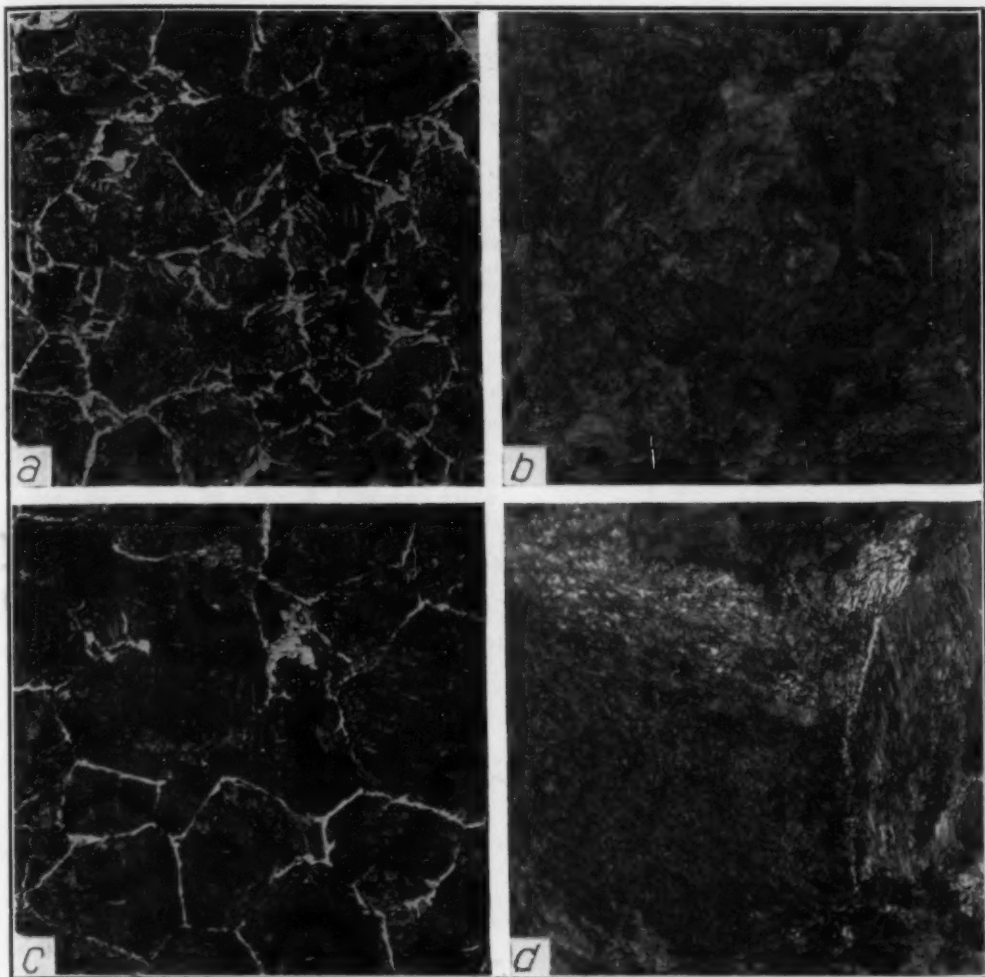
Fig. 3—Initial Structure of Experimental Plain Carbon Steels. (a) 0.48 Per Cent Carbon (PC-1). × 100. (b) 1.12 Per Cent Carbon (PC-2). × 500. (c) 0.57 Per Cent Carbon (GC-1). × 100. (d) 1.02 Per Cent Carbon (GC-2). × 500. Etched with 1 Per Cent Nital.

benzene vapor at 1700 degrees Fahr. and subsequently homogenizing by heating in vacuo at 1700 degrees Fahr. The hypoeutectoid steels had an initial structure of sorbite and ferrite (Figs. 3a and c) and the hypereutectoid steels had an initial structure of sorbite (Figs. 3b and d). The compositions of these steels are given in Table II.

RESULTS

High Purity Alloys of Iron and Carbon

In this group of alloys a comprehensive series of tests was made on the alloy containing 0.50 per cent carbon (HP-1). The grain size of this alloy at 1475, 1500, 1600, and 1800 degrees Fahr. (800,

Table III
Grain Size of Iron-Carbon Alloy HP-1 (0.50 Per Cent Carbon)

Temp. Degrees Fahr.	Rate of Heating Between 1325 and 1450 Degrees Fahr. Degrees F./min.	Grains/in.² at × 100	Remarks
1475	very rapid[1]	.....	Estimated A.S.T.M. grain #7.
1475	7.7	.....	Estimated A.S.T.M. grain #−2 to 1. Grains not outlined in approximately 20% of the area which consisted of coalesced ferrite and pearlite.
1500	very rapid[1]	35	
1500	440	12	
1500	200	4.3	
1500	190	2.5	
1500	170	3.5	
1500	155	4.4	
1500	13	.....	Estimated A.S.T.M. grain #1 or larger. Grains not outlined in approximately 30% of the area which consisted of coalesced ferrite and pearlite.
1500	3	.....	Estimated A.S.T.M. grain #1 or larger. Grains not outlined in approximately 70% of the area which consisted of coalesced ferrite and pearlite.
1600	very rapid[1]	50	
1600	940	12	
1600	470	9	
1600	325	9	
1600	280	7.3	
1600	100	1.2	
1600	80	2.5	
1600	10	0.4	
1600	3	1.0	
1800	very rapid[1]	5.4	
1800	1875	3.0	
1800	1875	2.3	
1800	1365	5.2	
1800	575	3.3	
1800	415	4.9	
1800	12	0.6	
1800	11	.....	Estimated A.S.T.M. grain #2.
1800	3	1.0	

[1]Heated in lead bath.

815, 870, and 980 degrees Cent.) was determined for widely varying rates of heating through the transformation range. The grain size of the alloy containing 1.01 per cent carbon (HP-2) was determined only at 1600 degrees Fahr. (870 degrees Cent.) and that of the alloy containing 1.21 per cent carbon (HP-3) was determined only at 1800 degrees Fahr. with various rates of heating. The results are summarized in Tables III, IV, and V. Representative micrographs are reproduced in Figs. 4 to 9, inclusive.

With the 0.50 per cent carbon alloy, the rate of heating through the transformation range had a very marked effect upon the grain size at all temperatures investigated below 1800 degrees Fahr. (980 degrees Cent.). The grain size increased with decrease in rate of heating. This trend was most pronounced in the upper range of

Table IV
Grain Size at 1600 Degrees Fahr. of Iron-Carbon Alloy HP-2 (1.01 Per Cent Carbon)

Rate of Heating Between 1325 and 1450 Degrees Fahr. Degrees F./min.	Grains/in.^{2} at $\times$100	Remarks
very rapid[1]	20	
very rapid[1]	20	
1070	..	Mixed grains—estimated 10% A.S.T.M. grain # 3-4 and 90% #7-8.
830	..	Mixed grains—estimated 10% A.S.T.M. grain # 3-4 and 90% #7-8.
625	12	
625	11	
625	15	
625	40	
580	12	
440	..	Mixed—noted all grains from A.S.T.M. grain #2 to 7. Few #2-3, majority #5.
420	10	Estimated A.S.T.M. grain #4-5.
400	..	
13	11	

[1]Heated in lead bath.

Table V
Grain Size at 1800 Degrees Fahr. of Iron-Carbon Alloy HP-3 (1.21 Per Cent Carbon)

Rate of Heating Between 1325 and 1450 Degrees Fahr. Degrees F./min.	Grains/in.^{2} at $\times$ 100
very rapid[1]	5.3
1875	3.2
1670	2.8
1670	2.7
1670	3.1
1360	3.7
1250	2.0
1250	2.3
1150	3.5
3	2.4
1.4	3.0

[1]Heated in lead bath.

heating rates, that is, after the rate of heating had decreased to a certain value, further decrease in rate caused but little increase in grain size of this alloy. At 1800 degrees Fahr., coarse grains (A.S.T.M. grain size 1 to 3) were produced regardless of the rate of heating through the transformation range. It should be pointed out, that the trend of increase in grain size with decrease in rate of heating also existed for the specimens heated at 1800 degrees Fahr.

With slow rates of heating coarse grains of the same order of magnitude were obtained at all temperatures. However, considerably coarser grains were produced at 1475, 1500, and 1600 degrees Fahr. with slow rates of heating than at 1800 degrees Fahr. with fast rates of heating.

The coarse grains produced at 1475 and 1500 degrees Fahr. in
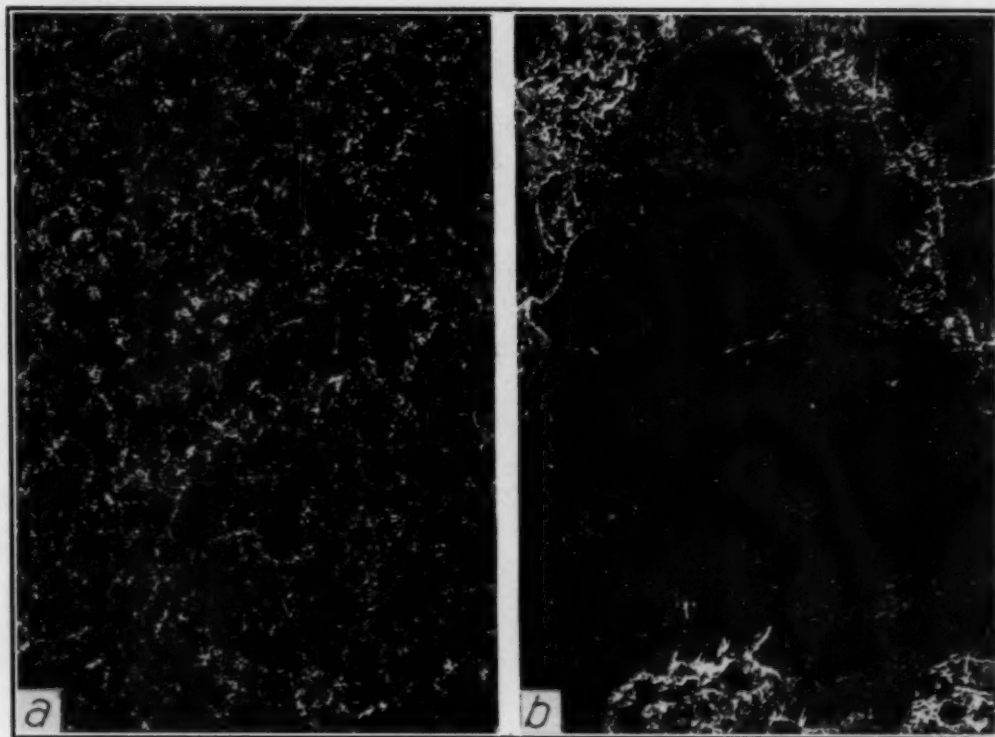
Fig. 4—Grain Size at 1475 Degrees Fahr. of Iron-Carbon Alloy HP-1 (0.50 Per Cent Carbon). (a) Heated in Lead Bath. Estimated A.S.T.M. Grain # 7. (b) Heated 7.7 Degrees Fahr. Per Minute. Estimated A.S.T.M. # —2 to 1. Grains Not Outlined in Approximately 20 Per Cent of the Area, Which Consisted of Coalesced Ferrite and Pearlite. Etched with 1 Per Cent Nital. × 100.

the 0.50 per cent carbon alloy with relatively slow rates of heating were found, upon cooling, to be associated with areas containing numerous ferrite and pearlite islands (Figs. 4b and 5d). The appearance, however, suggested that these were originally not mixed austenitic grains but that some of the large grains of the parent austenite had broken into many small grains of ferrite and pearlite. At 1500 degrees Fahr., this condition was noticeable for the specimen heated at the rate of 13 degrees Fahr. per minute (Table III and Fig. 5d); for the specimen heated at the still slower rate of 3 degrees Fahr. per minute this condition was considerably more marked. With slow rates of heating, specimens heated to 1600 and 1800 degrees Fahr. were also coarse-grained, but coalescence of ferrite and pearlite was not observed.

The results obtained for the 1.01 per cent carbon alloy at 1600 degrees Fahr. (Table IV and Fig. 8) showed that the finest grains were not obtained with the most rapid rate of heating. For example, approximately 20 grains per square inch at 100 diameters (A.S.T.M.
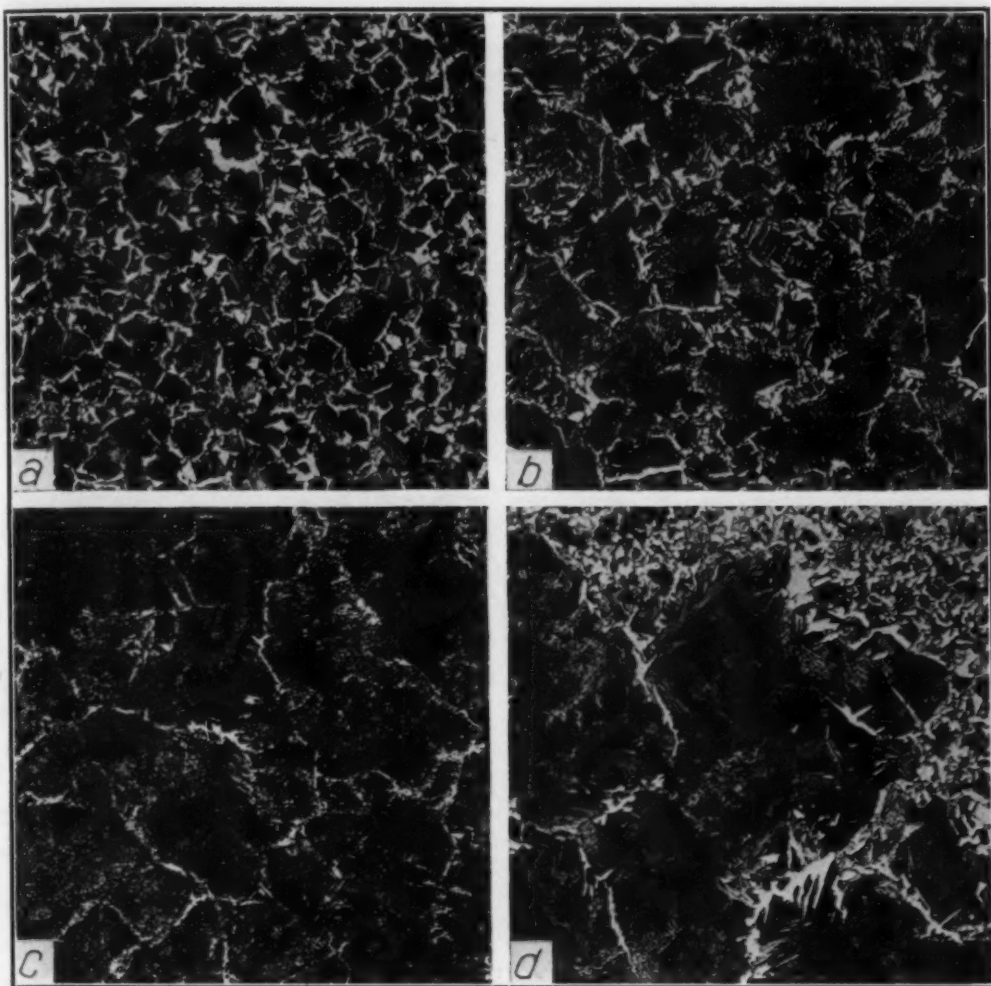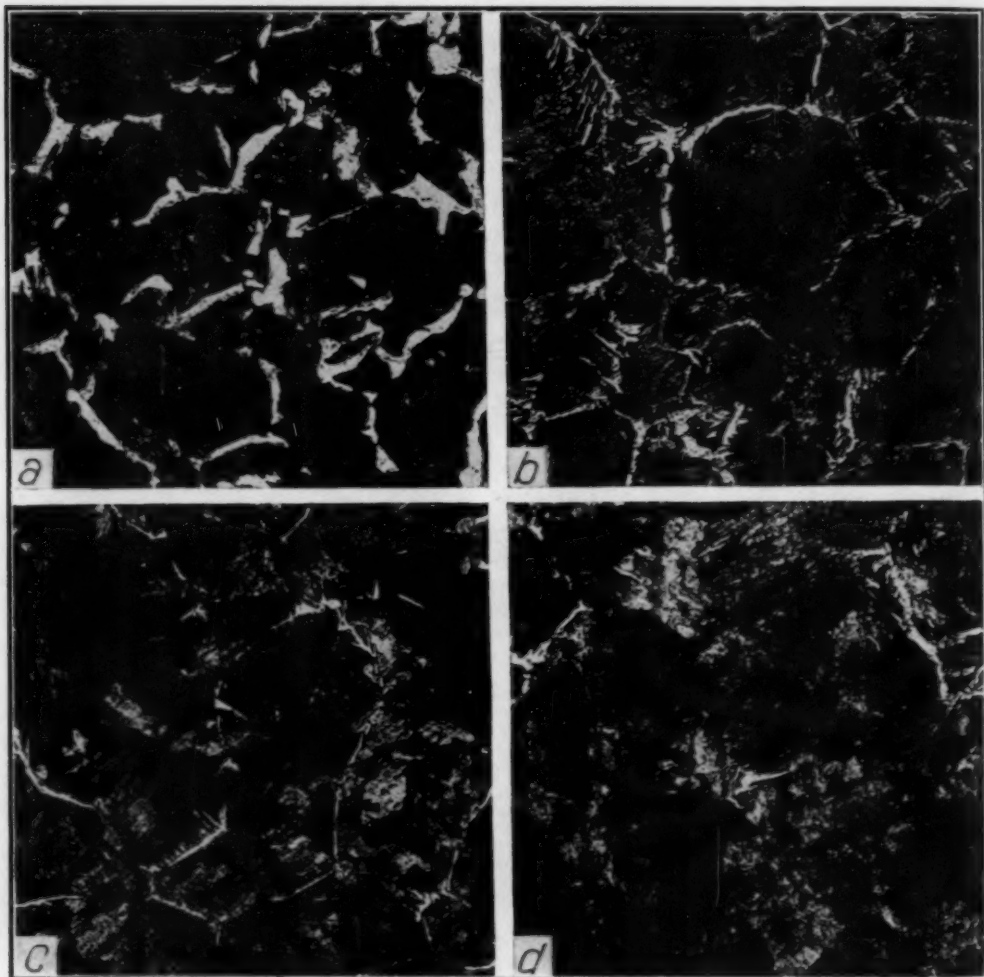
Fig. 5—Grain Size at 1500 Degrees Fahr. of Iron-Carbon Alloy HP-1 (0.50 Per Cent Carbon). (a) Heated in Lead Bath. 35 Grains Per Square Inch at × 100. (b) Heated 440 Degrees Fahr. Per Minute. 12 Grains Per Square Inch at × 100. (c) Heated 155 Degrees Fahr. Per Minute. 4.4 Grains Per Square Inch at × 100. (d) Heated 13 Degrees Fahr. Per Minute. Estimated A.S.T.M. Grain # 1 or Larger. Grains Not Outlined in Approximately 30 Per Cent of the Area, Which Consisted of Coalesced Ferrite and Pearlite. Etched with 1 Per Cent Nital. × 100.

grain size No. 5) were produced in specimens heated rapidly in a lead bath, whereas mixed grains, estimated at 10 per cent A.S.T.M. grain size No. 3 to 4 and 90 per cent No. 7 to 8, (not shown in Fig. 8) were produced by decreasing the heating rate to about 1000 degrees Fahr. per minute. Furthermore, there was an appreciable scatter in values of the grain sizes obtained when the rates were approximately constant and of the order of 625 degrees Fahr. per minute (Fig. 8b and c). These results suggest the possibility of the existence of a critical rate of heating through the transformation range that produces austenitic grains of minimum size. That is, larger grains may
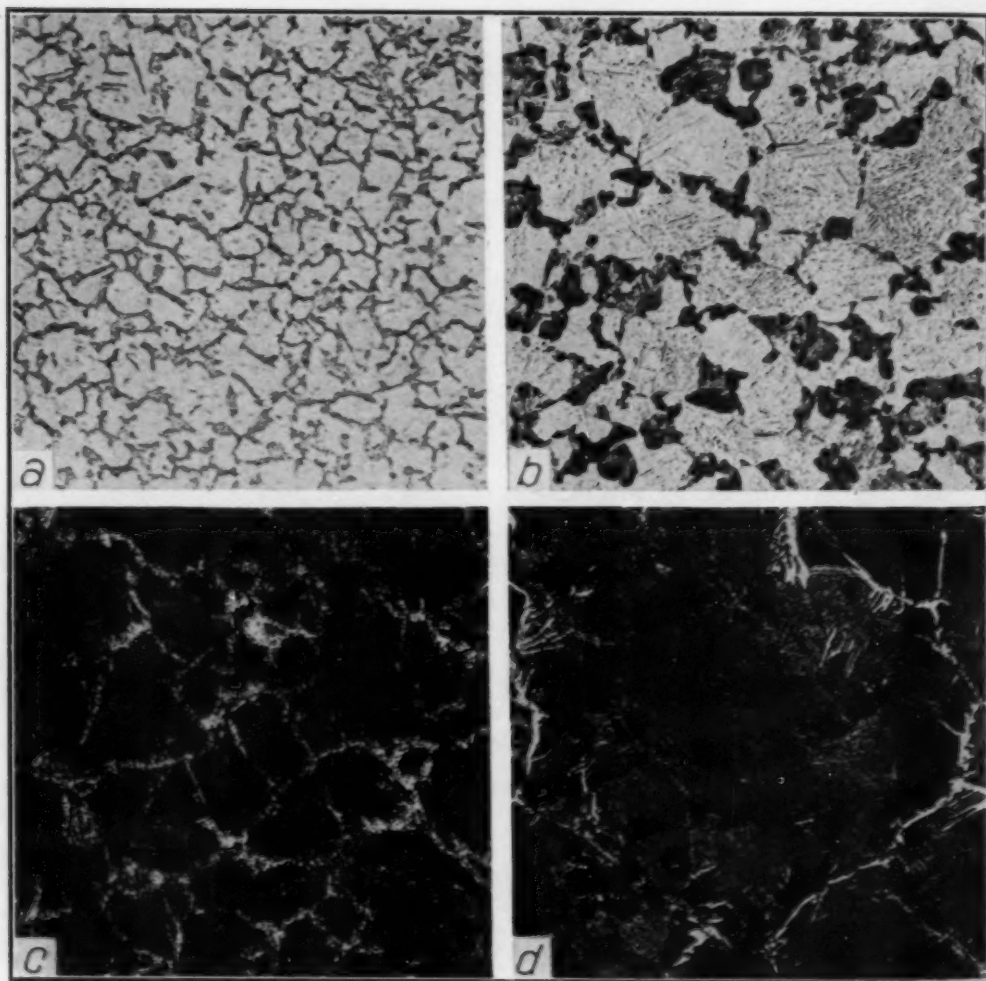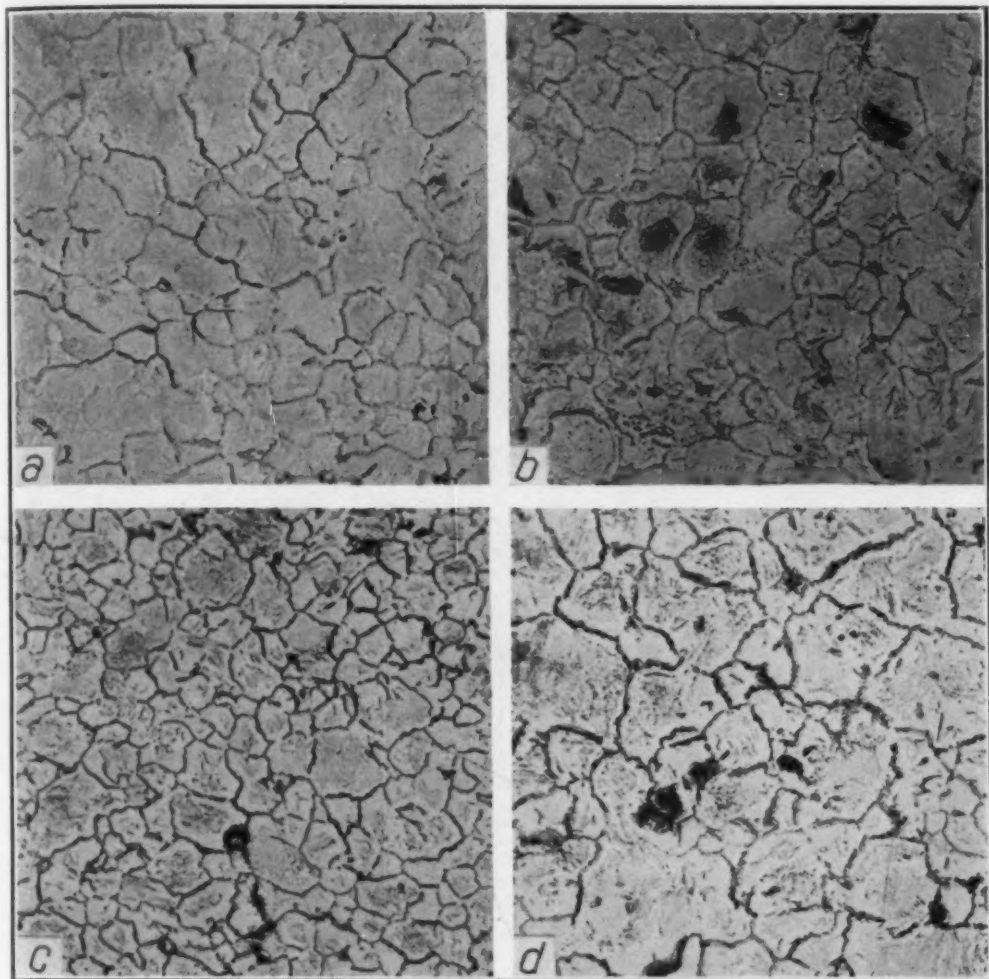
Fig. 6—Grain Size at 1600 Degrees Fahr. of Iron-Carbon Alloy HP-1 (0.50 Per Cent Carbon). (a) Heated in Lead Bath. 50 Grains Per Square Inch at × 100. (b) Heated 940 Degrees Fahr. Per Minute. 12 Grains Per Square Inch at × 100. (c) Heated 280 Degrees Fahr. Per Minute. 7.3 Grains Per Square Inch at × 100. (d) Heated 3 Degrees Fahr. Per Minute. 1 Grain Per Square Inch at × 100. Etched With 1 Per Cent Nital. × 100.

be produced when the heating rate is either faster or slower than the critical value.

The rate of heating through the transformation range had little effect on the grain size established at 1800 degrees Fahr. of the iron-carbon alloy containing 1.21 per cent carbon (Table V and Fig. 9).

The final austenitic grain size of these high purity alloys of iron and carbon was influenced by the rate of heating through the transformation range and by the maximum temperature to which the alloys were heated.

Commercial Plain Carbon Steels

It was believed that the general relation between rate of heating

Table VI
Grain Size of Steel C-1 (0.49 Per Cent Carbon "Noncontrolled")

Temp. Degrees F.	Rate of Heating Between 1325 and 1450° F. Degrees F. /Min.	Grains/in.² at × 100	Remarks
1475	Very rapid[1]	35	
1475	Very rapid[1]	45	
1475	Very rapid[1]	40	
1475	Very rapid[1]	45	
1475	Very rapid[1]	55	
1475	185	...	Estimated 40 per cent ASTM grain # 5-6; 60 per cent # 8.
1475	105	110	
1475	3.5	120	
1475	3.1	105	
1600	Very rapid[1]	30	
1600	Very rapid[1]	30	
1600	160	35	
1600	4	45	
1800	Very rapid[1]	6.1	
1800	Very rapid[1]	3.5	
1800	22	4.5	
1800	14	7.0	
1800	12	4.9	
1800	2.8	9.0	

[1]Heated in lead bath.

Table VII
Grain Size of Steel C-2 (0.49 Per Cent Carbon—"Controlled")

Temp. Degrees F.	Rate of Heating Between 1325 and 1450° F. Degrees F. /Min.	Grains/in.² at × 100	Remarks
1475	Very rapid[1]	..	Estimated 30 per cent ASTM grain # 5, 70 per cent # 8.
1475	Very rapid[1]	..	Estimated 60 per cent ASTM grain # 5-6, 40 per cent # 8.
1475	Very rapid[1]	75	
1475	Very rapid[1]	80	
1475	Very rapid[1]	80	
1475	41	..	Estimated 10 per cent ASTM grain # 7, 90 per cent #8.
1475	12	..	Estimated 15 per cent ASTM grain #6-7, 85 per cent # 8.
1475	2.7	120	
1600	Very rapid[1]	55	
1600	Very rapid[1]	90	
1600	13	..	Estimated 10 per cent ASTM grain #6, 90 per cent # 8.
1600	2.7	150	
1600	2.7	150	
1800	Very rapid[1]	25	
1800	Very rapid[1]	23	
1800	11	80	
1800	3.9	70	

[1]Heated in lead bath.
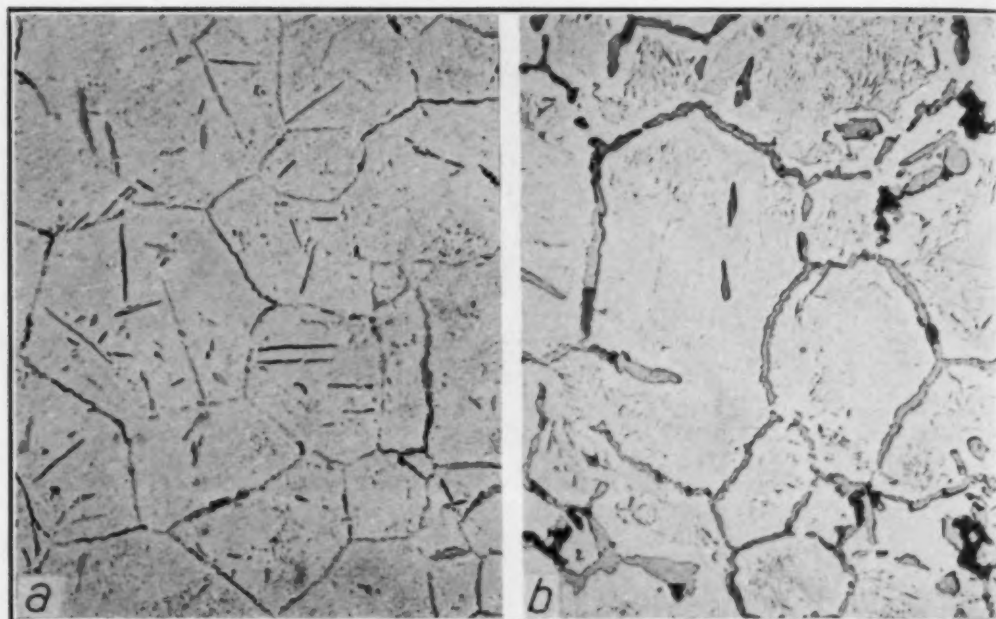
Fig. 7—Grain Size at 1800 Degrees Fahr. of Iron-Carbon Alloy HP-1 (0.50 Per Cent Carbon).   (a) Heated in Lead Bath.   5.4 Grains Per Square Inch at × 100.   (b) Heated 575 Degrees Fahr. Per Minute.   3.3 Grains Per Square Inch at × 100.   (c) Heated 11 Degrees Fahr. Per Minute.   Estimated ASTM Grain # 2.   (d) Heated 3 Degrees Fahr. Per Minute.   1 Grain Per Square Inch at × 100.   Etched with 1 Per Cent Nital.   × 100.

and grain size of commercial steels could be established by securing data on the effect of rate of heating on two hypo- and two hyper-eutectoid steels, one of which in each case had been treated to produce what is usually termed a "controlled" steel.   The results obtained are summarized in Tables VI, VII, VIII, and IX.   Representative micrographs of the grain sizes at different temperatures with various rates of heating are shown in Figs. 10 to 13, inclusive.

The rate of heating through the transformation range influenced the grain size established at 1475 degrees Fahr. (recommended hardening temperature) of the hypoeutectoid steels with both "non-controlled" and "controlled" grain size (Figs. 10a, 10b, and 11a, 11b)

Fig. 8—Grain Size at 1600 Degrees Fahr. of Iron-Carbon Alloy HP-2 (1.01 Per Cent Carbon). (a) Heated in Lead Bath. 20 Grains Per Square Inch at × 100. (b) Heated 625 Degrees Fahr. Per Minute. 15 Grains Per Square Inch at × 100. (c) Heated 625 Degrees Fahr. Per Minute. 40 Grains Per Square Inch at × 100. (d) Heated 13 Degrees Fahr. Per Minute. 11 Grains Per Square Inch at × 100. Etched with Boiling Sodium Picrate Solution. × 100.

and at 1600 and 1800 degrees Fahr. of the controlled steel (Figs. 11c, d, e, f). The rate of heating had no appreciable effect on the grain size at 1600 and 1800 degrees Fahr. of the "noncontrolled" steel (Figs. 10c, d, e, f). Regardless of the rate of heating, both of these steels were fine-grained at 1475 degrees Fahr., and the "controlled" steel was fine-grained at 1600 degrees Fahr.

Under conditions in which the grain size was influenced by the rate of heating these commercial 0.49 per cent carbon steels, the minimum size grains were not obtained with the maximum rate of heating. That is, in these steels the grain size tended to increase with increase in rate of heating. This trend is contrary to that ob-

Fig. 9—Grain Size at 1800 Degrees Fahr. of Iron-Carbon Alloy HP-3 (1.21 Per Cent Carbon). (a) Heated in Lead Bath. 5.3 Grains Per Square Inch at × 100. (b) Heated 3 Degrees Fahr. Per Minute. 2.4 Grains Per Square Inch at × 100. Etched with Boiling Sodium Picrate Solution. × 100.

Table VIII
Grain Size of Steel C-3 (1.05 Per Cent Carbon—"Noncontrolled")

Temp. Degrees F.	Rate of Heating Between 1325 and 1450° F. Degrees F./Min.	Grains/In.^{2} at × 100
1650	Very rapid[1]	20
1650	750	26
1650	9	18
1650	3	16
1800	Very rapid[1]	5.3
1800	Very rapid[1]	4.9
1800	9	5.2
1800	3.6	5.9

[1]Heated in lead bath.

served in the high purity alloy of iron and carbon having a similar carbon content.

The rate of heating had no significant effect on the grain size at 1650 and 1800 degrees Fahr. of the noncontrolled steel containing 1.05 per cent carbon (Table VIII and Fig. 12). With the controlled steel, the rate of heating influenced the grain size at both 1650 and 1800 degrees Fahr. (900 and 980 degrees Cent.). At the lower temperature, the coarsest grains were obtained with an intermediate rate of heating (Table IX). Slow rates of heating produced grains of the same order of magnitude as very rapid rates (Figs. 13a and
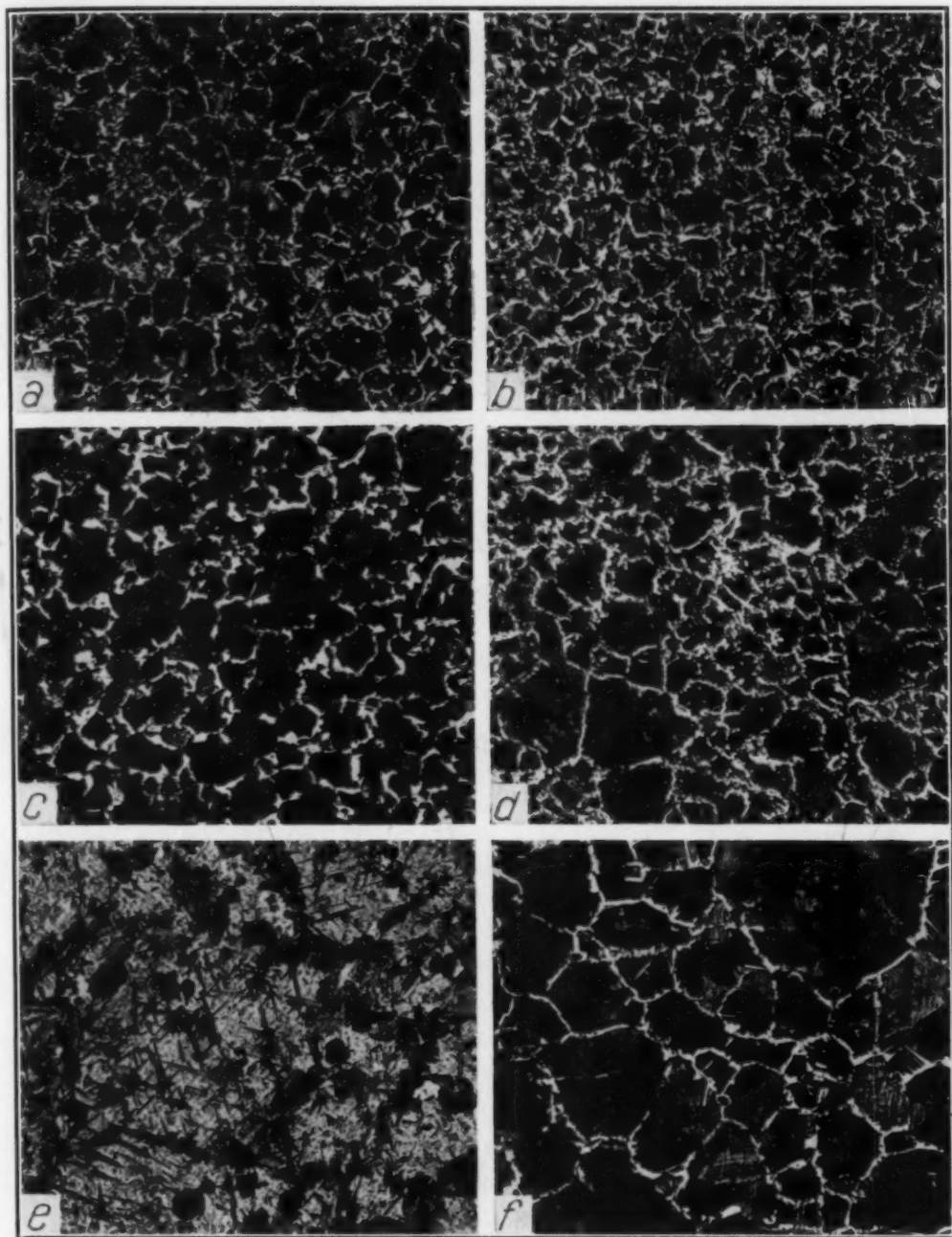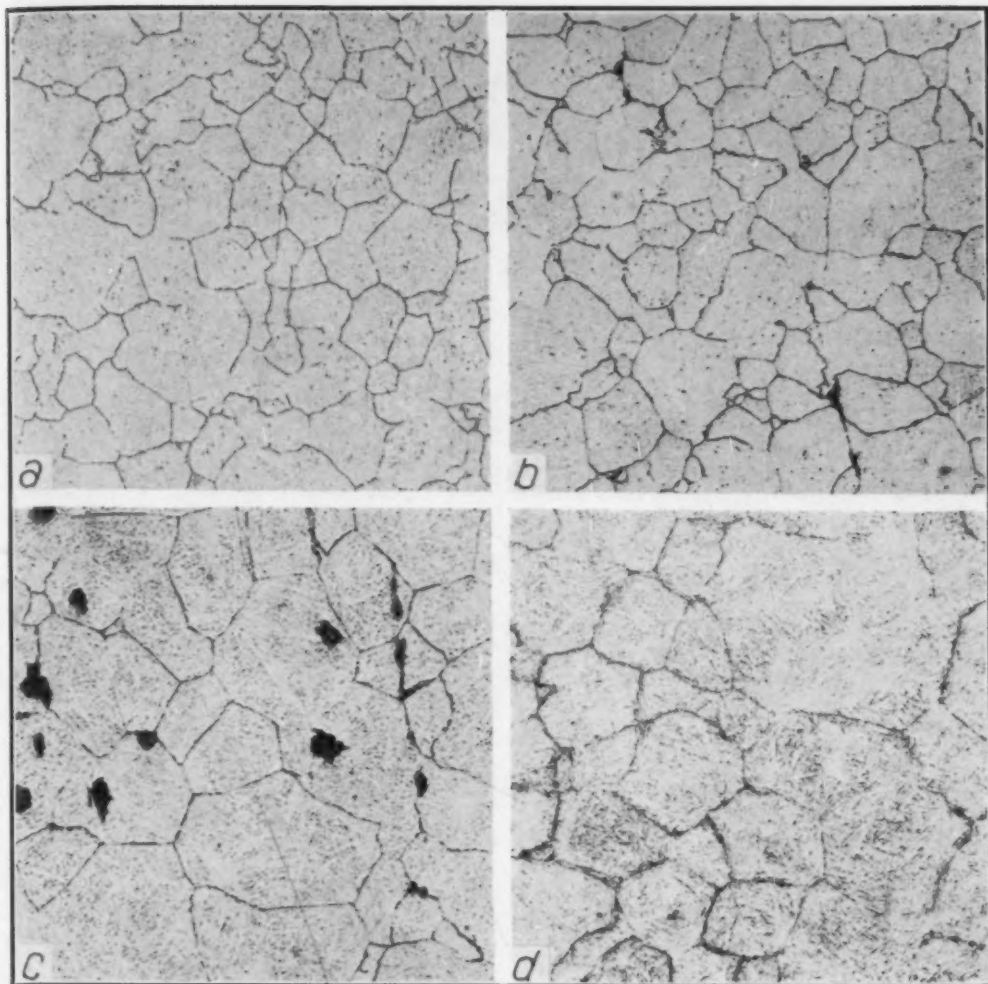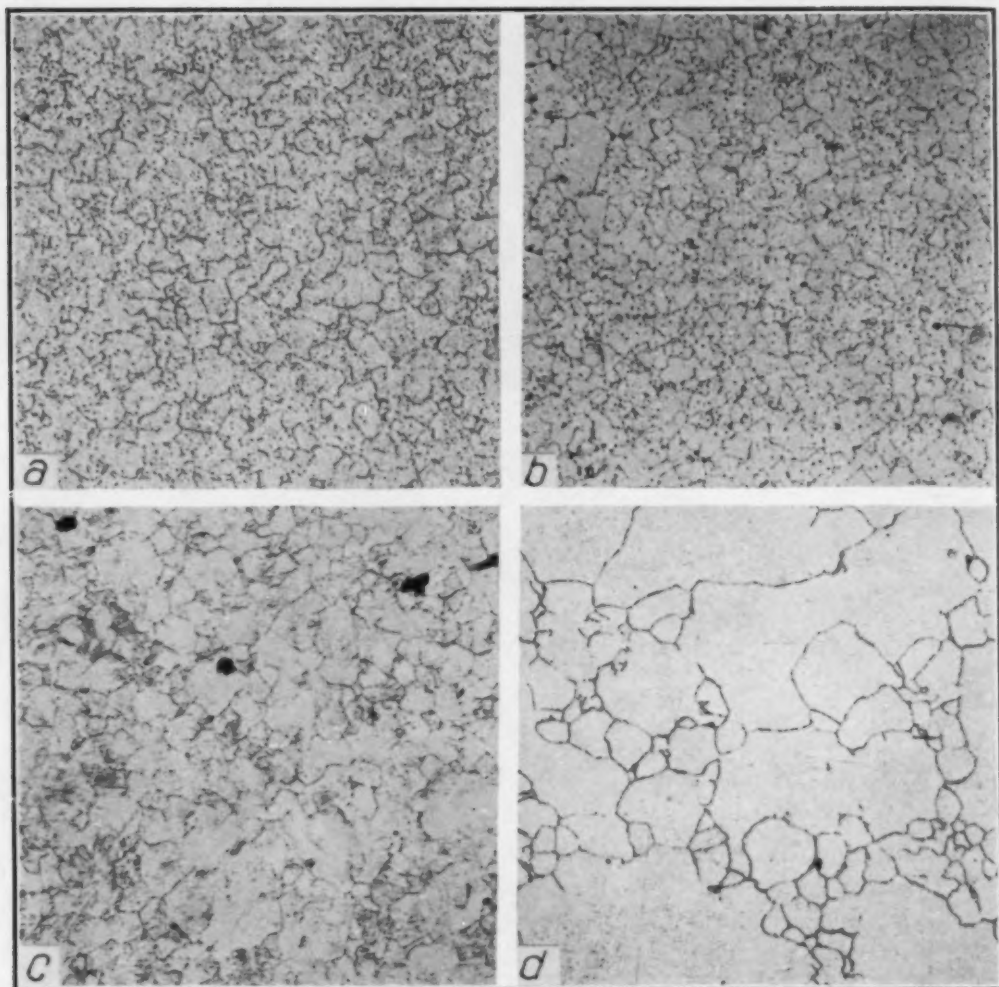
Fig. 10—Grain Size at Different Temperatures of Commercial Steel C-1 (0.49 Per Cent Carbon—"Noncontrolled" Grain Size. (a) 1475 Degrees Fahr.   Heated in Lead Bath. 35 Grains Per Square Inch at × 100. (b) 1475 Degrees Fahr. Heated 3.1 Degrees Fahr. Per Minute. 105 Grains Per Square Inch at × 100. (c) 1600 Degrees Fahr. Heated in Lead Bath. 30 Grains Per Square Inch at × 100. (d) 1600 Degrees Fahr. Heated 4 Degrees Fahr. Per Minute. 45 Grains Per Square Inch at × 100. (e) 1800 Degrees Fahr. Heated in Lead Bath. 6.1 Grains Per Square Inch at × 100. (f) 1800 Degrees Fahr. Heated 2.8 Degrees Fahr. Per Minute. 9 Grains Per Square Inch at × 100.   Etched with 1 Per Cent Nital. × 100.

b).   At 1800 degrees Fahr., the grain size of this steel increased with decrease in rate of heating (Figs. 13c and d), a trend similar to that shown by the 0.50 per cent carbon alloy and contrary to that of
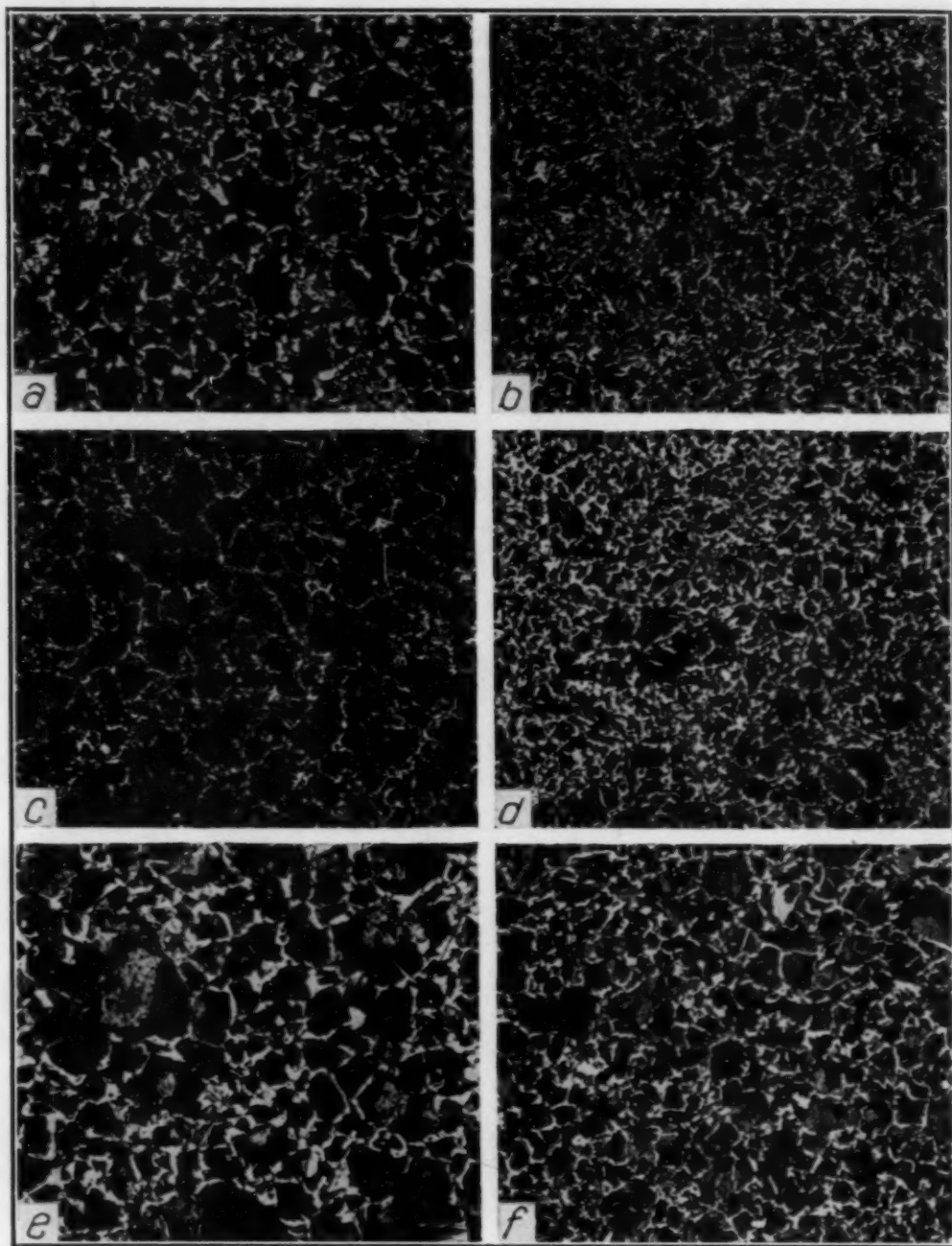
Fig. 11—Grain Size at Different Temperatures of Commercial Steel C-2 (0.49 Per Cent Carbon—"Controlled" Grain Size). (a) 1475 Degrees Fahr. Heated in Lead Bath. 80 Grains Per Square Inch at × 100. (b) 1475 Degrees Fahr. Heated 2.7 Degrees Fahr. Per Minute. 120 Grains Per Square Inch at × 100. (c) 1600 Degrees Fahr. Heated in Lead Bath. 55 Grains Per Square Inch at × 100. (d) 1600 Degrees Fahr. Heated 2.7 Degrees Fahr. Per Minute. 150 Grains Per Square Inch at × 100. (e) 1800 Degrees Fahr. Heated in Lead Bath. 25 Grains Per Square Inch at × 100. (f) 1800 Degrees Fahr. Heated 3.9 Degrees Fahr. Per Minute. 70 Grains Per Square Inch at × 100. Etched with 1 Per Cent Nital. × 100.

the commercial hypoeutectoid steels. These results obtained with commercial plain carbon steels, both "noncontrolled" and "controlled",

Fig. 12—Grain Size at Different Temperatures of Commercial Steel C-3 (1.05 Per Cent Carbon—"Noncontrolled" Grain Size). (a) 1650 Degrees Fahr. Heated in Lead Bath. 20 Grains Per Square Inch at × 100. (b) 1650 Degrees Fahr. Heated 3 Degrees Fahr. Per Minute. 16 Grains Per Square Inch at × 100. (c) 1800 Degrees Fahr. Heated in Lead Bath. 5.3 Grains Per Square Inch at × 100. (d) 1800 Degrees Fahr. Heated 3.6 Degrees Per Minute. 5.9 Grains Per Square Inch at × 100. Etched with 1 Per Cent Nital. × 100.

show that in certain heats the austenitic grain sizes established at various temperatures were sensitive to the rate of heating through the transformation range. In other heats, the grain sizes were insensitive to the rate of heating. The cause of the observed variations cannot be definitely stated at this time.

Experimental Plain Carbon Steels

It is apparent that the effect of rate of heating on the grain size of the iron-carbon alloys was different from the effect on commercial plain carbon steels. Since the preparation of the iron-carbon alloys

Fig. 13—Grain Size at Different Temperatures of Commercial Steel C-4 (1.06 Per Cent Carbon—"Controlled" Grain Size). (a) 1650 Degrees Fahr. Heated in Lead Bath. 90 Grains Per Square Inch at × 100. Etched with 1 Per Cent Nital. × 100. (b) 1650 Degrees Fahr. Heated 9 Degrees Fahr. Per Minute. 110 Grains Per Square Inch at × 100. Etched with Boiling Sodium Picrate. × 100. (c) 1800 Degrees Fahr. Heated in Lead Bath. 95 Grains Per Square Inch at × 100. Etched with Boiling Sodium Picrate and 1 Per Cent Nital. × 100. (d) 1800 Degrees Fahr. Heated 2.8 Degrees Fahr. Per Minute. Estimated 25 Per Cent ASTM Grain # 7, 25 Per Cent # 4, and 50 Per Cent # 1. Etched with 1 Per Cent Nital. × 100.

was different from that of the commercial steels, it was thought the procedure used in preparing the alloys might have had some influence on the relation between the heating rate and grain size. Specimens were available of both hypo- and hypereutectoid steels prepared from a 0.2 per cent carbon steel (aluminum-killed) by pack carburizing and by gas carburizing as described in a previous section of this report. If the method of introduction of carbon (gas carburizing) were responsible for the differences observed in the grain sizes of the iron-carbon alloys with various rates of heating, it was thought

Table IX
Grain Size of Steel C-4 (1.06 Per Cent Carbon—"Controlled")

Temp. Degrees F.	Rate of Heating Between 1325 and 1450° F. Degrees F. /Min.	Grains/in.^{2} at × 100	Remarks
1650	Very rapid[1]	90	
1650	Very rapid[1]	85	
1650	940	40	
1650	9	110	
1800	Very rapid[1]	95	
1800	Very rapid[1]	95	
1800	9	13	
1800	8.6	..	Estimated 25 per cent ASTM grain # 6-8, 15 per cent # 4-5, 60 per cent # 1 or larger.
1800	2.8	..	Estimated 25 per cent ASTM grain # 7, 25 per cent # 4, 50 per cent # 1.

[1]Heated in lead bath.

Table X
Grain Size at 1600 Degrees Fahr. of Experimental Steels

Steel	Rate of Heating Between 1325 and 1450° F. Degrees F. /Min.	Grains /In.^{2} at × 100	Remarks
PC-1 (0.48 Per Cent Carbon)	Very rapid[1]	45	
PC-1 (0.48 Per Cent Carbon)	10	..	Estimated 15 per cent ASTM grain # 2-3, 15 per cent # 4, 70 per cent # 7-8.
PC-2 (1.12 Per Cent Carbon)	Very rapid[1]	15	Few grains ASTM grain # 2-3 and 7.
PC-2 (1.12 Per Cent Carbon)	Very rapid[1]	16	Few grains ASTM grain # 2-3 and 7.
PC-2 (1.12 Per Cent Carbon)	17	..	Estimated ASTM grain # 4.
PC-2 (1.12 Per Cent Carbon)	17	16	
GC-1 (0.57 Per Cent Carbon)	Very rapid[1]	..	Estimated about 60 per cent ASTM grain # 2-4, 40 per cent # 7-8.
GC-1 (0.57 Per Cent Carbon)	11	..	Estimated 50 per cent ASTM grain # 2-4, 50 per cent # 7-8.
GC-2 (1.02 Per Cent Carbon)	Very rapid[1]	14	
GC-2 (1.02 Per Cent Carbon)	Very rapid[1]	14	
GC-2 (1.02 Per Cent Carbon)	7	11	

[1]Heated in lead bath.

that perhaps a similar relation would be shown in the carburized steels.

The grain size established at 1600 degrees Fahr. with various rates of heating was determined for the experimental steels containing about 0.5 and 1 per cent carbon. The results of the grain size measurements are summarized in Table X. These data and the representative photomicrographs (Figs. 14 and 15) show that the rate of heating had no significant effect on the grain size at 1600 degrees Fahr. of any of these steels.
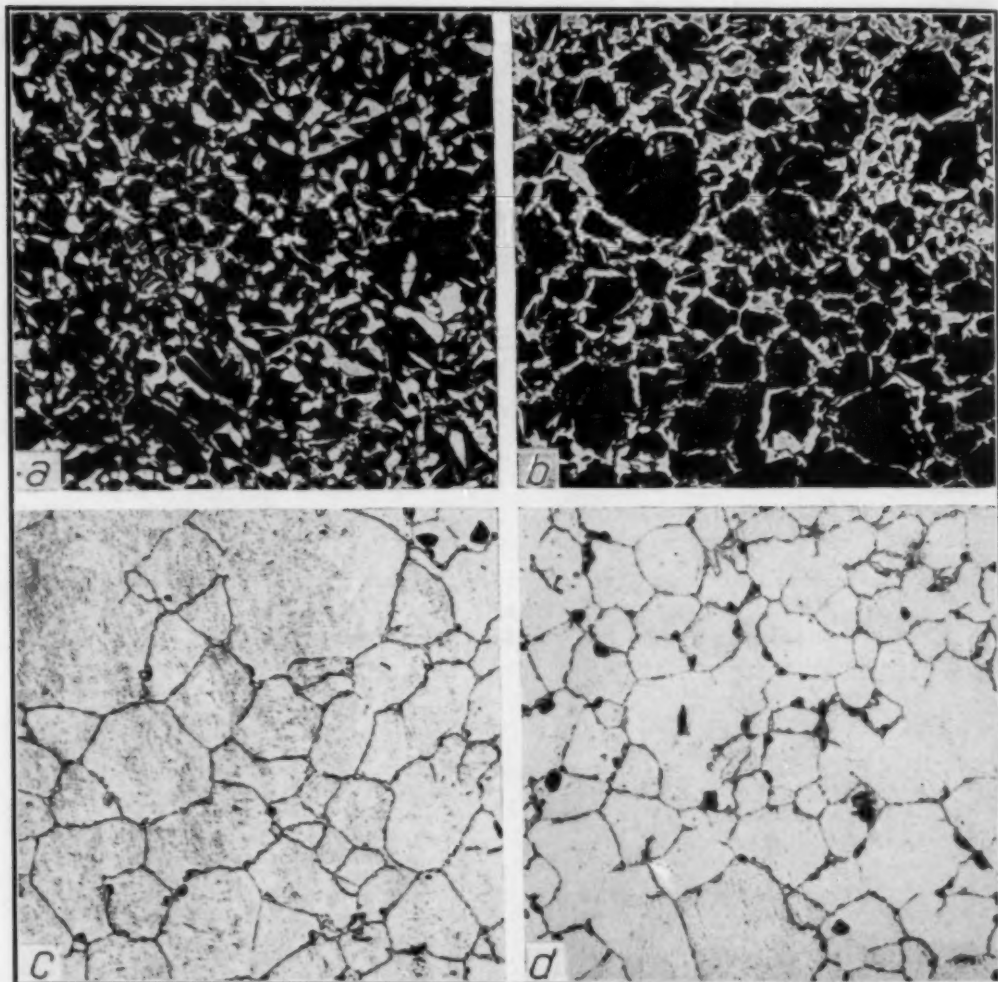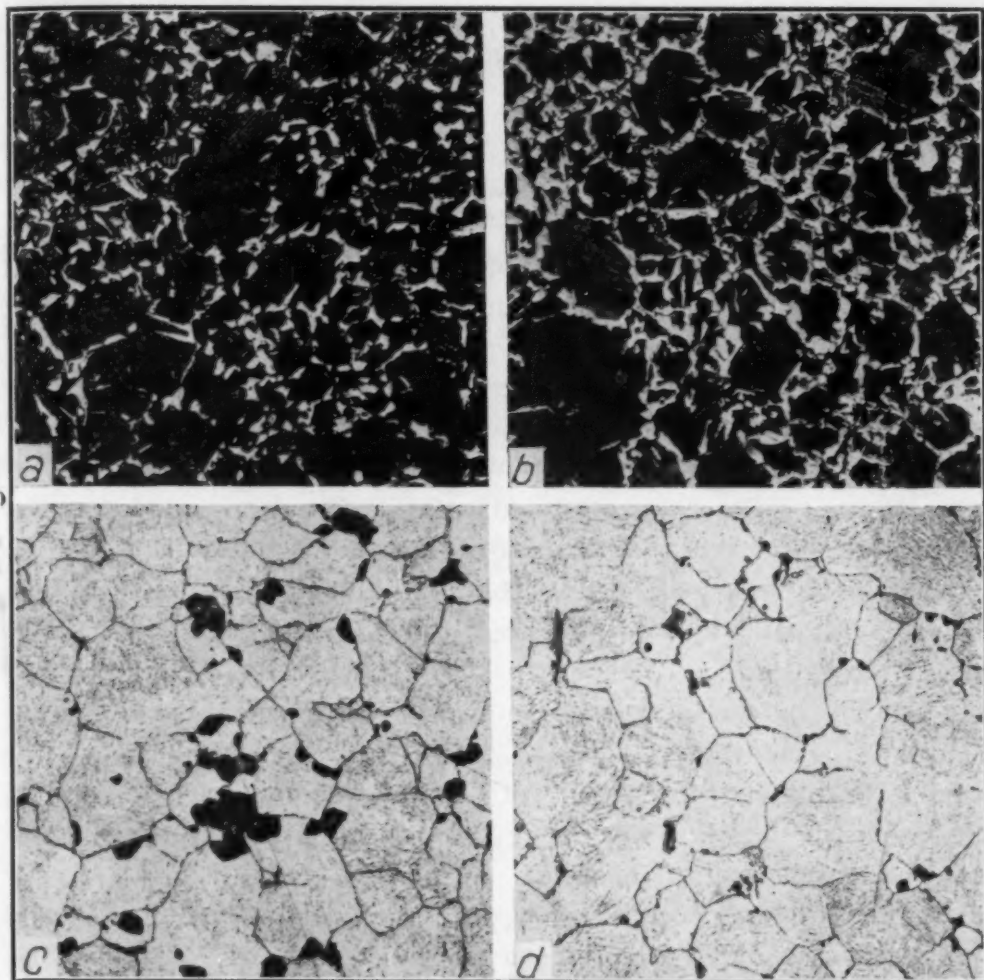
Fig. 14—Grain Size at 1600 Degrees Fahr. of Experimental Plain Carbon Steels (Packed Carburized). (a) PC-1 (0.48 Per Cent Carbon). Heated in Lead Bath. 45 Grains Per Square Inch at × 100. (b) PC-1 (0.48 Per Cent Carbon). Heated 10 Degrees Fahr. Per Minute. Estimated 15 Per Cent ASTM Grain # 2 to 3, 15 Per Cent # 4, and 70 Per Cent # 7 to 8. (c) PC-2 (1.12 Per Cent Carbon). Heated in Lead Bath. 15 Grains Per Square Inch at × 100. (d) PC-2 (1.12 Per Cent Carbon). Heated 17 Degrees Fahr. Per Minute. 16 Grains Per Square Inch at × 100. Etched with 1 Per Cent Nital. × 100.

The results obtained with the experimental steels indicate that the variations in grain size with rate of heating of the high purity alloys of iron and carbon cannot be attributed solely to the method by which carbon was introduced.

SUMMARY

The austenitic grain size established at different temperatures with various rates of heating through the transformation range was determined for high purity alloys of iron and carbon, and for com-

Fig. 15—Grain Size at 1600 Degrees Fahr. of Experimental Plain Carbon Steels (Gas Carburized). (a) GC-1 (0.57 Per Cent Carbon). Heated in Lead Bath. Estimated 60 Per Cent ASTM Grain # 2 to 4, 40 Per Cent # 7 to 8. (b) GC-1 (0.57 Per Cent Carbon). Heated 11 Degrees Fahr. Per Minute. Estimated 50 Per Cent ASTM Grain # 2 to 4, 50 Per Cent # 7 to 8. (c) GC-2 (1.02 Per Cent Carbon). Heated in Lead Bath. 14 Grains Per Square Inch at × 100. (d) GC-2 (1.02 Per Cent Carbon). Heated 7 Degrees Fahr. Per Minute. 11 Grains Per Square Inch at × 100. Etched with 1 Per Cent Nital. × 100.

mercial and experimental steels which had a wide range in carbon content. The commercial steels also differed in the method of deoxidation.

For the high purity alloys of iron and carbon containing 0.50 per cent carbon, the grain size at 1475, 1500, and 1600 degrees Fahr. increased with decrease in rate of heating, whereas the grain size at 1800 degrees Fahr. was not so noticeably dependent upon the rate of heating. Coarser grains were produced at the lower temperatures with slow rates of heating than at higher temperatures with fast rates of heating. With slow rates of heating, grains of the same

order of magnitude (coarse grains) were obtained at all temperatures.

With the high purity alloy of iron and carbon containing 1.01 per cent carbon, the grain size at 1600 degrees Fahr. increased but slightly with decrease in rate of heating. There were indications that for this alloy there is a critical rate of heating at which rate the finest grains were obtained.

With the high purity alloy of iron and carbon containing 1.21 per cent carbon, the rate of heating had no significant effect on the grain size at 1800 degrees Fahr.

The rate of heating influenced the grain size at 1475 degrees Fahr. of the commercial 0.49 per cent carbon steels with both "noncontrolled" and "controlled" grain size, and at 1600 and 1800 degrees Fahr. of the "noncontrolled" steel. The grain size of these steels tended to increase with increase in rate of heating.

With the "noncontrolled" steel containing 1.05 per cent carbon, the rate of heating had no significant effect on the grain size at 1650 and 1800 degrees Fahr. With the "controlled" steel of similar carbon content, the grain size at 1650 and 1800 degrees Fahr. was influenced by the rate of heating. At the lower temperature, the coarsest grains were produced with an intermediate rate of heating, whereas at the higher temperature the coarsest grains were produced with the slowest rate of heating.

With the experimental steels, containing approximately 0.5 and 1 per cent carbon, the grain size at 1600 degrees Fahr. was not affected by the rate of heating.

The data presented in this report show that, in certain cases, the austenitic grain size of high purity alloys of iron and carbon and plain carbon steels is affected by the rate of heating through the transformation range; i.e., the grain size of some of these materials is sensitive to the rate of heating. All the materials, however, did not respond in the same manner. In view of these findings it is necessary, when making grain size specifications, that consideration be given to the possible effects that the rate of heating through the transformation range may have upon the grain size of the steels under consideration.

References

1. T. G. Digges, "Influence of Austenitic Grain Size on the Critical Cooling Rate of High-Purity Iron-Carbon Alloys," *Journal Research,* NBS, Vol. 24, 1940, p. 723, RP1308.
2. N. F. Ward and J. E. Dorn, "Grain Size of Steel—a Critical Review," *Metals & Alloys,* Vol. 10, 1939, p. 74, 115, 212, 246.
3. Carl Shapiro, "What About Grain Size?", *Iron Age,* Vol. 143, 1939, March 16, p. 25; March 30, p. 23; April 6, p. 33.
4. M. A. Grossmann, "Grain Size in Metals, with Particular Reference to Grain Growth in Austenite," TRANSACTIONS, American Society for Metals, Vol. 22, 1934, p. 861.
5. T. G. Digges and Louis Jordan, "Hardening Characteristics and Other Properties of Commercial One Per Cent Carbon Tool Steels," *Journal Research* NBS, Vol. 15, 1935, p. 385, RP837. Also "Hardening Characteristics of One Per Cent Carbon Tool Steels," TRANSACTIONS, American Society for Metals, Vol. 23, 1935, p. 839.
6. H. Tobin and R. L. Kenyon, "Austenitic Grain Size of Eutectoid Steel," TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 133.
7. C. H. Herty, Jr., D. L. McBride and S. O. Hough, "The Effect of Deoxidation on Grain Size and Grain Growth in Plain Carbon Steels." Cooperative Bulletin 65, Mining and Metallurgical Investigations, Carnegie Institute of Technology and Mining and Metallurgical Advisory Boards, 1934.
8. T. G. Digges, "Effect of Carbon on the Critical Cooling Rate of High-Purity Iron-Carbon Alloys and Plain Carbon Steels," *Journal Research* NBS, Vol. 20, 1938, p. 571, RP1092. Also, "Effect of Carbon on the Hardenability of High-Purity Iron-Carbon Alloys," TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 408.

DISCUSSION

Written Discussion: By Carl L. Shapiro, technical director, Lynnwood Laboratories, Inc., Newark, New Jersey.

It is indeed gratifying to see such truly scientific work done by the authors in clearing up a lot of suppositions concerning the austenitic grain size of steel. Work of this type is not only timely but lays a foundation for future progress.

The austenitic grain size and the mechanical and thermal treatments which influence it may be ascertained by two methods: (1) physical and (2) chemical. The physical method of determining the austenitic grain size consists of noting the influence of the various factors upon the physical properties and structural characteristics of the material involved. The limitations of this method are that the results are always qualitative.

In the writer's opinion, the chemical method of determining the grain size of steel offers more pertinent and quantitative information than the physical method. When these two methods are combined, a true picture of the characteristics and properties of any aggregate can be visualized.

One method of determining the grain size of iron and steel is the Eggertz colorimetric method for determination of combined carbon, which is known in the mill or laboratory as the "color carbon test". This old well-known test has been advocated for many years by the late esteemed Professor Albert Sauveur. This method offers correlations between grain size and carbide particle size. This test is also extremely sensitive to all the factors which tend to influence

the physical properties of the aggregate, such as aging, heat treatment, working, etc., since these factors first change the structural characteristics of the aggregate, which in turn influence the physical properties of the metal. The chemical method, represented by any volumetric method of analysis, may be used to determine not only the size of the carbide particles but also the particle size of any compound-forming element in steel such as nitrogen, sulphur, phosphorus, etc. These results can be noted in any volumetric test since the rate of dissolution under normal conditions, such as constant time, temperature, and acid concentration, is a function of particle size.

It is to be hoped that Messrs. Rosenberg and Digges will continue their excellent work upon grain size in the future by both the physical and chemical methods of examination.

Written Discussion: By Harry Tobin, research laboratories, American Rolling Mill Co., Middletown, Ohio.

The authors are to be congratulated for the large number of well presented data showing the effect of heating rate through the transformation range on austenitic grain size. These data should be a great help in the control of the austenitic grain size of steel where a wide range of heating rates must be used.

I wish to comment on the authors' conclusions concerning the effect of the heating rate through the critical temperature on the grain size at 1600 and 1800 degrees Fahr. (870 and 980 degrees Cent.). At these temperatures, I believe that the austenitic grain growth characteristics of the steel are a greater factor in the establishment of the final grain size than the heating rate through the critical. Although the authors held the sample only 15 minutes at the maximum temperatures, I have found that in some steels which have no grain growth inhibitors, the grains grew from one to two A.S.T.M. numbers in the first fifteen minutes at temperatures of 1600 or 1800 degrees Fahr. (870 or 980 degrees Cent.). This may account for the fact that the high purity alloy of iron and carbon, the noncontrolled steel and the experimental steels which had no grain growth inhibitors showed no respective differences in grain size at the higher temperatures regardless of heating rates through the critical.

In Table III it is shown that at 1500 and 1600 degrees Fahr. (815 and 870 degrees Cent.) the grains are smaller as the heating rate through the critical temperature is increased. At 1500 degrees Fahr. (815 degrees Cent.) with a heating rate of 440 degrees Fahr. (227 degrees Cent.) per minute, the grains per square inch are 12, but at 1600 degrees Fahr. (870 degrees Cent.) with a heating rate of 940 degrees Fahr. (505 degrees Cent.) or more than double the rate at 1500 degrees Fahr. (815 degrees Cent.) the grains per square inch are still 12. Thus the grains were not reduced in size with an increase in heating rate through the critical. This implies that the effects of the heating rates are destroyed if the steel is heated to its coarsening range. Furthermore the slower heating rates are equivalent to a prolonged holding at the maximum temperature.

Although the data presented show that the rate of heating through the critical range affects the grain size, the steel was held at the maximum temperature for a short time. My experience has been that differences in grain size after heating through the critical temperature are minimized or eliminated when the soaking time is longer.

Oral Discussion

R. L. KENYON:[1] There is a point I would like to mention. Although the heating rate is defined as the rate through a range of 1325 to 1450 degrees Fahr., it generally is experimentally difficult to maintain that same rate at higher temperatures. For example, it may require considerable time to bring the specimen up to a temperature as high as 1800 degrees Fahr. and effectively that is the same as a longer soak at the higher temperature, which may be near or at the coarsening range. So effectively, conditions are different from the assumed heating rate through a range of 1350 to 1450 degrees Fahr.

C. E. SIMS:[2] This discussion recalls some work done several years ago at Battelle and discussed by Dorn and Harder before this Society in 1937 on the effect of various factors in producing coarse- or fine-grained structures in steels.

There are two theoretical factors that play a part in the growth of grains which may be pertinent to this discussion. The first is that one grain can grow only by encroaching on its neighbor. In other words, the larger grains swallow up small ones to become still larger.

Now it may be presumed that if all the grains got off to an even start none would have an advantage over the others and there could be no grain growth. If, however, the transformation is irregular and some austenite grains form earlier than others, the first ones would be larger and because of the lower surface energy would absorb the smaller ones. In the fast rate of heating there would tend to be a mass transformation with all of the steel transforming simultaneously which would result in an austenite containing uniformly small grains. Grain growth under this condition would be very slow.

The second factor which inhibits grain growth is apparently a mechanical barrier in the grain boundaries which prevents diffusion across the boundaries and thus quite effectively prevents grain growth, until the barrier is removed by dissolution. It is well known that these so-called fine-grained steels can be changed to coarse-grained steels with appropriate treatment, and one of the phenomena reported by Dorn and Harder was that long-continued heating just below the lower critical or at about 1250 degrees Fahr. (675 degrees Cent.) had an important effect on the subsequent grain size. In other words, if a steel was held for a long time at 1250 degrees Fahr. (675 degrees Cent.) and then heated up through the critical the grain size was very different as compared to one that was heated up without holding at the subcritical temperature.

I am wondering if some of the differences found by the authors were due to heating before the steel reached the critical temperature?

The theory advocated by Dorn and Harder to explain the grain growth inhibition contemplates a substance with unknown identity which has a solid solubility that varies with temperature. It also stipulates a change in solubility at the critical temperature so that the solubility curve roughly approximates the temperature-dilatation curve. This means that when steel transforms from alpha to gamma iron the drop in solubility causes a precipitation and the precipitate gathers in the grain boundaries of the newly formed austenite

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grains. The barrier thus set up prevents grain growth until a temperature is reached at which the material redissolves after which grain growth proceeds.

Considerable circumstantial evidence was found to substantiate this theory; for example, two steels heated at 1250 degrees Fahr. (675 degrees Cent.) for a long period of time, one quickly cooled and the other cooled with extreme slowness, had different grain size characteristics on subsequent heating above the critical. The first was fine-grained and the second coarse-grained. The tentative explanation for this was that in the first case the soluble substance was held in supersaturation by the fast cooling while in the second case the slow cooling allowed it to precipitate in relatively coarse particles. During the subsequent heating these coarse particles did not have time to redissolve and so were not in a position to precipitate on the austenite grain boundaries.

This might explain why the controlled grain size steels are coarser in fast heating than with slow heating through the critical. If the experiments were conducted in such a way that there was no difference in the heating time in the subcritical range then the explanation might be as follows:

Fast heating through the critical temperature range might cause the transformation to take place so rapidly that there would not be time for diffusion of the precipitating material to the austenite boundaries and the barriers would be incomplete. The slower heating would enable the precipitation to take place entirely in the grain boundaries which would result in well formed barriers and more complete inhibition of grain growth.

This is offered only as a suggestion with the hope that it might throw a little light on the present problem.

J. R. VILELLA:[a] The fact that heating rate influences the austenite grain size of steel has been observed from time to time at our laboratory. Our observations were always confined to commercial grades of steels, and for that reason these remarks refer only to commercial grades studied by the authors. Our observations are in perfect agreement with those reported in this paper, that is, increasing the heating rate tends to coarsen the austenite grains but the degree of coarsening varies considerably between different heats. No instance of refinement of the austenite grains as a result of fast heating was observed.

We also observed that the temperature to which the steel is heated is another important factor. By this I mean that the coarsening effect of rapid heating is more pronounced the nearer the heating temperature approaches that at which the steel coarsens on normal or slow heating.

Authors' Closure

The authors wish to thank all those who have contributed to the discussion of this paper.

It is the authors' opinion that the Eggertz method to which Dr. Shapiro refers may be used as a procedure for determining the carbide particle size in steel and not the actual austenitic grain size. It is quite possible, of course, that the carbide particle size might have an appreciable influence upon the austenitic grain size. Other factors, such as time at maximum temperature,

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[a]United States Steel Corporation Research Laboratory, Kearny, N. J.

initial structure, etc., which also might influence the austenitic grain size, were not investigated. As stated in the text, the present study was confined solely to the influence of the rate of heating to different temperatures on the austenitic grain size. The suggestion offered by Dr. Shapiro, however, is an excellent one and correlation between carbide particle size and austenitic grain size undoubtedly would be of value.

It is well known, as Messrs. Tobin and Kenyon point out, that time at temperature has an important effect upon the final austenitic grain size, particularly at the higher temperatures. Whether this factor has a more important effect than the rate of heating on the grain size of the steels investigated can be determined only by further experiments. The specific instance mentioned by Mr. Tobin wherein the high purity iron-carbon alloy containing 0.50 per cent carbon had the same grain size at both 1500 and 1600 degrees Fahr. (815 and 870 degrees Cent.) (Table III of the text), although the rate of heating was twice as rapid in the latter case, serves to emphasize that the rate of heating had a marked influence on the austenitic grain size of this alloy at these temperatures. Thus, it would be expected that the grain size at 1600 degrees Fahr. (870 degrees Cent.) would be coarser than at 1500 degrees Fahr. (815 degrees Cent.). In this particular case the grain size established at 1600 degrees Fahr. (870 degrees Cent.) by heating more rapidly was no coarser than that established at 1500 degrees Fahr. (815 degrees Cent.) with a slower rate of heating. Although it has been already stated in the text, attention is again directed to the fact that in this particular alloy, with very slow rates of heating, coarser austenitic grains were obtained at 1475 and 1500 degrees Fahr. than at 1800 degrees Fahr. with rapid rates. It is also significant that the grain size obtained at 1800 degrees Fahr. with slow rates of heating was no coarser than the grain size obtained at 1475 and 1500 degrees Fahr. (800 and 815 degrees Cent.) with similar rates of heating.

Obviously, as pointed out by Messrs. Kenyon and Sims, if considerable time is consumed in heating to the maximum temperature, this might have some influence on the austenitic grain size. The authors realize that the procedure used did not insure precisely the same rate of heating in the subcritical range for all specimens. For the slower rates of heating, the time in the subcritical range often required an appreciable proportion of the complete heating cycle. In some cases this time might have been sufficient to allow some spheroidization of the initial structure and thus to indirectly influence the austenitic grain size by change in carbide particle size or rate of solution of the carbides. This is a worthy point and deserves further study. However, the time required to heat from 1450 degrees Fahr. (790 degrees Cent.) to the test temperature was small in comparison with the 15 minutes that the small specimens were held at the test temperature.

The authors are pleased to have their test results confirmed by the observations of Mr. Vilella in that the austenitic grain size of commercial steels is influenced by the rate of heating through the transformation range and the degree of coarsening varies between different heats.

A BALANCED PROTECTIVE ATMOSPHERE—ITS PRODUCTION AND CONTROL

By J. R. Gier

Abstract

This paper describes the production and use of a balanced protective atmosphere for controlling the surface carbon content of steels during heat treatment. A new device for measuring the relative carbon pressure of furnace atmospheres is described. Experiments are reported showing how this device can be used in preadjusting the composition of furnace atmospheres to chemical equilibrium with the carbon in any steel.

Introduction

FURNACE atmospheres now commonly used for protection of steel during heat treatment have a definite tendency to carburize or decarburize because they are not in chemical equilibrium with the carbon in the steel. Attempts to adjust these atmospheres to the required balance generally give erratic results because the gas components are not in mutual equilibrium with one another.

Changes in surface carbon of steel from this cause are most rapid in reducing atmospheres commonly used in bright hardening furnaces. In fact, experience has shown that there is actually less surface damage produced on some steels by heating them in a slightly oxidizing atmosphere than in an unbalanced reducing gas.

A satisfactory solution of the problem would be provided by a balanced reducing gas that is capable of the necessary accurate composition control. Such an atmosphere has been developed and is now in industrial use. This improved atmosphere is called "endogas" controlled atmosphere, so named because it is produced by the endothermic reaction of hydrocarbon fuel with air in an electrically heated catalyst. This gas is completely formed in a reaction chamber then delivered directly to the furnace. It requires no further processing such as removing CO_2 and water vapor which are present only in the small amounts required for maintaining the gas in balance, according to the law of mass action.

A distinctive characteristic of endogas is that it can be adjusted to a chemical balance with steel of any carbon content. This adjustment is possible because the gas is a thoroughly reacted mixture in which the active components are in mutual equilibrium. Regulation of the gas is accomplished by varying the proportions of the air-fuel feed mixture to the generator.

To prevent changes of surface carbon in the steel requires that the carbon pressure of the furnace atmosphere match that of the steel being treated. The carbon pressure of the steel is a function of its carbon content and temperature while the carbon pressure of the gas is determined by the proportions of its active components. Quantitatively the balancing of the carbon in steel with that of gas is a delicate process; this is because the CO_2 content, which is the controlling factor, must be present in minute but definite amounts usually too small to measure or even detect by chemical analysis.

Few, if any, controlled atmospheres now in use are capable of being adjusted in composition to this precise balance. Moreover, there has been no means available for measuring carbon pressure to aid in making this adjustment. After it had been demonstrated that endogas could be controlled with precision, there was evident need for an indicator of its carbon pressure so that the gas could be regulated to the carbon in the steel being protected.

Present indicating devices for atmospheres are responsive to the heat of combustion or thermal conductivity of a gas; but these properties have no definite relation to carbon pressure, which is the property of chief concern in a gas for protecting steels, therefore the usefulness of these devices is limited accordingly. To supply this need a device has been developed for measuring the carburizing character of a gas; it is directly responsive only to the carbon pressure of a gas regardless of its composition, thermal conductivity or heat of combustion.

This device is known as a hot wire carbon gage. It employs a thin steel wire electrically heated to incandescence in the test gas for a few minutes while a carbon equilibrium determined by gas carbon pressure is attained between the gas and the wire. Cutting off the current allows the wire to "gas quench" and retain the carbon in a martensitic structure. Measurement of the electrical resistance of the wire, which is a sensitive function of its carbon content, then can be used as a measure of the carbon pressure of the gas after the relation between resistance and carbon pressure has been experi-

mentally determined under standardized conditions. This gage is simple, accurate and adaptable to shop use.

In the following sections the preparation and use of endogas are described and its characteristics discussed. The construction and operation of the hot wire gage are explained and experiments are reported which illustrate its use in controlling the carbon pressure of endogas.

CHARACTERISTICS OF A BALANCED GAS

Mixtures of air and hydrocarbon fuel have long been used in various ways to make protective furnace atmospheres but the usual experience with them is that they tend to decarburize steel completely or to carburize it to saturation, apparently having no intermediate quality. For this reason atmospheres are generally designated as being "carburizing" or "decarburizing" in the above extreme sense. There has been justification for classifying gases this way because there is only slight difference in composition between a gas mixture in equilibrium with a high carbon steel and one in equilibrium with a low carbon steel. This is illustrated by Table I, in which are listed several typical endogas analyses and the corresponding carbon content of steels in equilibrium with these mixtures at 1700 degrees Fahr. (925 degrees Cent.). The experimental procedure for determining these values is described later. It should be noted that for a medium or higher carbon content steel the CO_2 is too low for measurement by ordinary means.

Table I
(Gas components are in per cent by volume).

H_2O	CO_2	CO	H_2	CH_4	N_2	Per Cent Carbon in Steel at 1700 Degrees
1.80	0.4	19.7	35.7	0.7	43.5	0.20
0.50	0.0	20.1	39.3	0.5	40.1	0.64
0.26	0.0	20.4	39.0	0.7	39.9	0.94
0.13	0.0	20.6	38.6	0.9	39.9	1.34

A brief reference to the physical chemistry of the gas-metal reactions pertaining here may be helpful in getting a clear picture of the fundamental principle of this protective gas and its control.

Carburization and decarburization of steel may be represented by the reaction (Fe, C) $+ CO_2 \rightleftarrows$ Fe $+ 2$ CO, consisting of two separate reactions:

$$(Fe, C) \rightleftarrows Fe + C \tag{1}$$

$$2\,CO \rightleftarrows CO_2 + C \tag{2}$$
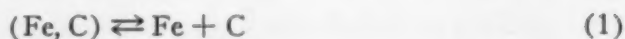
where the term (Fe, C) represents a solid solution of iron and carbon which may be regarded as exerting an immeasurably small but definite carbon pressure;* this carbon pressure being a direct function of the amount of carbon in the steel and its temperature. It may be assumed that in the gas phase there also exists a carbon pressure in equilibrium with the CO and CO_2. The amount of this carbon pressure in the gas phase may be expressed according to the mass action law as:

$$[C] = k_2\,\frac{[CO]^2}{[CO_2]} \tag{3}$$

where k_2 is the equilibrium constant of reaction (2). In a gas mixture where other active components such as H_2, H_2O, and CH_4 are present in equilibrium their effect is to control the relative concentrations of CO and CO_2 by interaction with them according to the mass action law and thereby control the carbon pressure of the mixture.

If a change in carbon content of steel is to be prevented during heat treatment it is necessary that the carbon pressure of the furnace atmosphere be maintained equal to that of the steel. When these carbon pressures are not equal a transfer of carbon will occur from the phase having the higher pressure to that having the lower pressure. The rate of carbon transfer between hot steel and a gas is a direct function of the difference between their respective carbon pressures and of the temperature.

From the foregoing discussion it appears that the essential characteristics of a satisfactory protective atmosphere for steel which is made from hydrocarbon gases is that it be capable of control of carbon pressure within the required limits. The type of gas herein described has this important characteristic. It is prepared with simple equipment as described in the following section.

PREPARATION AND CHARACTERISTICS OF ENDOGAS

The generator for producing endogas is essentially an electrically heated reaction chamber containing a catalytic mass through which the fuel mixture is passed. Here the hydrocarbon compounds are decomposed and reacted with the oxygen and moisture of the air.

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*The term "carbon pressure" of steel is used here to mean fugacity or escaping tendency; as applied to a gas it means carbon forming tendency.

The process is endothermic and will not proceed to equilibrium unless the catalytic action is completely effective.

A layout of the laboratory apparatus is shown in Fig. 1. A mixing pump draws air and natural gas through the flow gages and delivers the mixture to the generator. In the present experi-
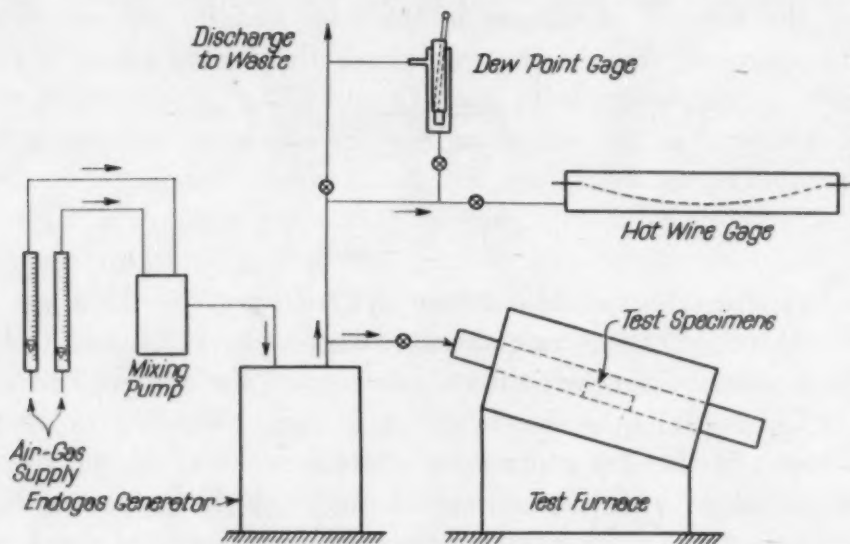
Fig. 1—Schematic Sketch of Layout of Laboratory Apparatus.

ments the product gas was produced at 200 cubic feet per hour. Of this volume a flow of 20 cubic feet per hour was put through a test furnace and 5 cubic feet per hour each through the hot wire gage and a dew point gage; the balance being discharged to waste.

The test furnace has a 2½ inch I.D. silica tube heating chamber; this extends beyond the furnace body at one end to provide a zone for cooling the specimens in the gas. The test specimens were moved in and out on a light metal tray. The test gas was let in at the upper end and discharged past a loose fitting brick plug at the lower end where it was burned.

By varying the air-gas feed ratio of the endogas generator the carbon pressure of the product gas can be adjusted to balance the carbon pressure of any steel. Fig. 2 shows how the feed ratio (with Pittsburgh natural gas fuel) is related to the equilibrium carbon content of steel heated to 1700 degrees Fahr. (925 degrees Cent.) in the corresponding gas. Values for this curve were experimentally determined by heating thin strips of steel in the gas until no further change of carbon occurred. They were then rapidly cooled in the gas and the carbon determined.

The test specimens used in this work were Swedish spring steel 0.006 x 1⅜ x 4 inches containing initially 1.2 per cent carbon. These were carefully weighed before and after treatment and the final carbon content was calculated by change in weight. A heating period
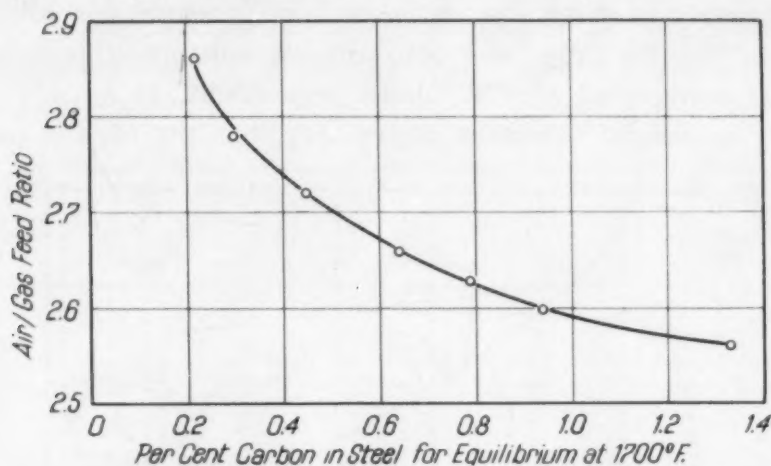
Fig. 2—Equilibrium Carbon Content of Steel at 1700 Degrees Fahr. Versus Air/Gas Feed Ratio of Endogas Generator.

of about one hour was required to reach a carbon equilibrium although periods of two hours or more were used. Two or more specimens were treated at one time to confirm the results.

Fig. 3 shows the relation between water vapor content of this particular type of gas and the equilibrium carbon content of the steel specimens for this same series of tests. Water vapor in limited amount is essential to the equilibrium between the gas components. This curve applies only to a gas mixture of 20 per cent CO, 40 per cent H_2 and 40 per cent N_2. Other proportions of H_2 and CO would alter the position of the curve.

It should be mentioned here that endogas can be prepared from any type of fuel gas but of course the air-gas ratios for a given carbon pressure will vary for different gases.

Evidence of a true carbon equilibrium between the steel and the gas was obtained when two specimens of the same steel having widely different carbon contents were heated together at 1700 degrees Fahr. (925 degrees Cent.) in the same gas. They were 0.006 inch thick spring steel; initially one contained 1.2 per cent carbon and the other had been completely decarburized in wet hydrogen previous to this test. After heating them for two hours in endogas and rapidly cooling them in the cooling zone of the test furnace they were found to have the same carbon content of 0.64 per cent as determined

by calculation from change in weight during heating. Although this result was expected it was nevertheless interesting to observe its actual happening.

It should be noted that steels heated in the two-phase austenite-ferrite region will have the same carbon pressure for all carbon contents within this range at a constant temperature; this is because the carbon content of this austenite is constant. It is only in the completely austenitic condition above Ac_3 that the carbon pressure
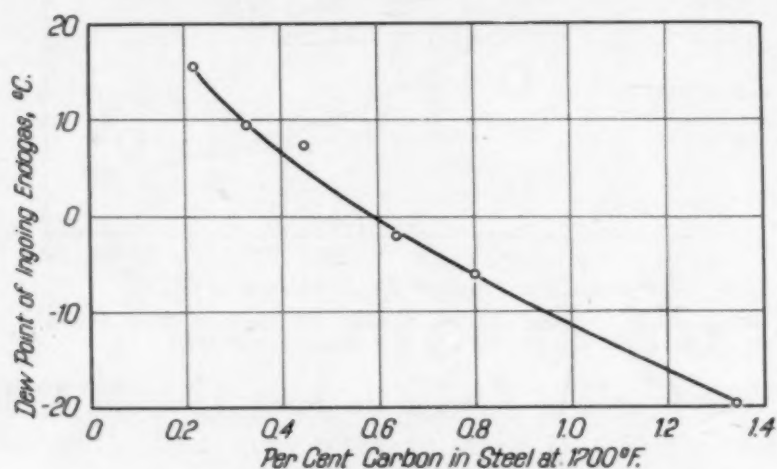
Fig. 3—Relation Between Dew Point of Endogas and the Carbon Content of Steel Heated to 1700 Degrees Fahr. in this Gas.

of a steel will be a definite function of its carbon content. However, carbon pressure is always a function of temperature regardless of the number of phases present.

In order to determine the optimum temperature for the generator and also the effect of generator temperature on carbon pressure tests were run with a constant feed ratio. As before, thin steel specimens were heated in the test furnace at 1700 degrees Fahr. (925 degrees Cent.) in endogas until equilibrium had occurred. Fig. 4 shows how the equilibrium carbon content varied with generator temperature at a constant feed ratio. It appears that in the range between 1700 and 1800 degrees Fahr. (925 and 980 degrees Cent.) the generator temperature has only a minor effect on the carbon pressure of the product gas. Below 1700 degrees Fahr. (925 degrees Cent.) the sharp dropping off of the curve is probably due to incomplete gas reaction. The reason for the upturn in the curve above 1800 degrees Fahr. (980 degrees Cent.) is not yet understood.

It has been shown that this gas is inherently capable of ad-

justment to chemical balance with steel of any carbon content by simply regulating the feed ratio within narrow limits. However, when the gas is used in industrial furnaces its control is complicated somewhat by contaminating gases diffusing from the brickwork of the furnace. These tend to increase the H_2O and CO_2 and thereby lower the carbon pressure of the furnace atmosphere relative to the inlet gas.
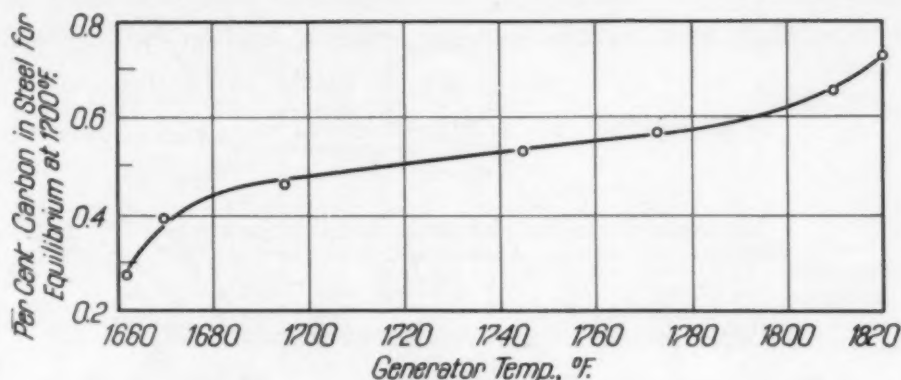
Fig. 4—Effect of Generator Temperature on Carbon Pressure of Endogas with Constant Feed Ratio.

Effects of contamination in the furnace can be largely offset by increasing the carbon pressure of the inlet gas and by having an adequate flow of gas through the furnace. Experience has shown that for short cycle heating in this gas its activity is low enough to allow considerable margin of variation in carbon pressure without harmful results to the steel. For example, certain areas of an S.A.E. 1020 part were case carburized and the part was then heated for hardening in an endogas atmosphere having a carbon pressure in balance with a medium carbon steel. After heating one hour at 1550 degrees Fahr. (845 degrees Cent.) and water quenching, the carburized areas were file hard and the uncarburized areas were soft enough to machine easily. Thus, for short heating periods a medium carbon pressure will accommodate steels having a considerable carbon range.

Carbon pressure being such an important factor in the behavior of protective gases, it is imperative that this quality be measured and controlled, if uniformly good heat treating results are to be obtained. Since it is a complex quality of a gas that cannot be evaluated satisfactorily by ordinary chemical analysis a need was recognized for a device that would be responsive to carbon pres-

sure and serve as a measure of its value. Such a device was developed in the form of the hot-wire gage described in the following section.

Hot Wire Gage Construction

The purpose of this gage is to evaluate quickly and directly the carbon pressure of furnace atmospheres so that they can be controlled with greater precision. In principle it involves the heating of a thin steel wire in the test gas until a carbon equilibrium is
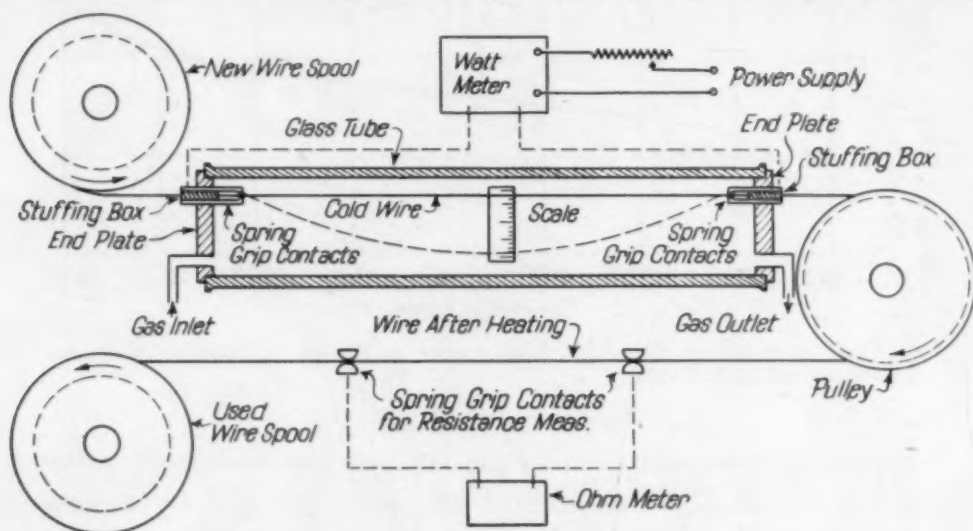
Fig. 5—Schematic Sketch of the Hot Wire Gage.

established between the gas and the wire. This requires only a few minutes after which the wire is rapidly cooled to retain its carbon in solid solution as martensite. The electrical resistance and certain other physical properties of the wire after this treatment under standardized conditions can then be used as a measure of the carbon content of the wire which, in turn, measures the carbon pressure of the gas. By means of this gage the quality of the furnace atmosphere can be quickly determined at any time and preadjusted to suit the carbon content of the steel being treated so that no change in surface carbon will occur.

Fig. 5 shows a schematic sketch of the hot wire gage. It consists of a glass tube 2-inch diameter by 14 inches long with two spring contacts spaced 12 inches apart mounted in the end plates closing the ends of the tube. The test wire, made of 0.007-inch diameter low carbon steel, fed from a spool enters one end of the tube through a stuffing box, a 12-inch section of the wire in the tube is suspended

between the two spring contacts. The wire passes out the opposite end of the tube through a second stuffing box; it goes over pulley, then back through spring contacts and is finally wound on spool. A vertical metal scale is placed at the center of the tube close to the plane of the wire to measure its sag.

A power source of adjustable voltage is connected through a wattmeter to the section of wire suspended in the glass tube between the electrodes. An ohmmeter is connected to the external contacts—
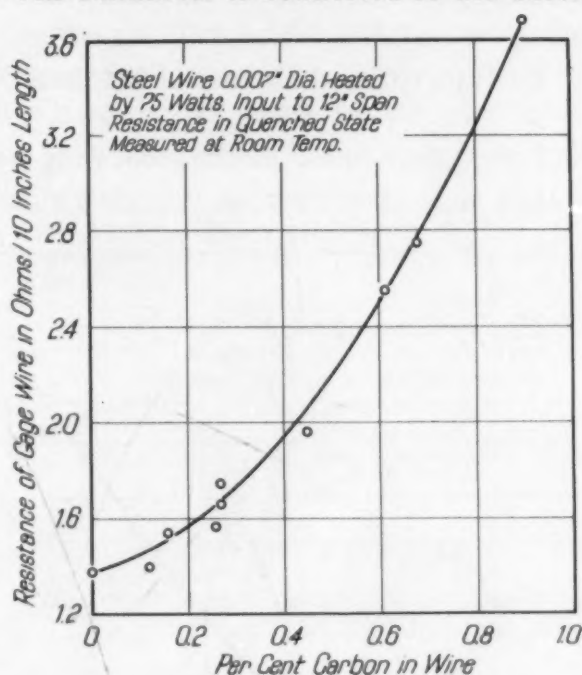
Fig. 6—Resistance of Carbon Gage Wire Versus Carbon Content of Gage Wire.

to measure at room temperature the resistance of the section of wire stretched between them.

To use the gage a small flow (5 cubic feet per hour) of the gas to be tested is passed through the glass tube. The wire is heated to some arbitrarily chosen temperature above 1700 degrees Fahr. (925 degrees Cent.) applying the necessary wattage to it. After 10 minutes at temperature in the gas the power is shut off and the portion of the wire that had been heated is advanced to a position between the external contacts where its resistance is measured at room temperature. The gage wires used for these experiments was plain low carbon steel containing 0.5 per cent manganese.

Gage wires were analyzed for carbon after this treatment and the carbon content of the wire is plotted against its resistance in the

curve of Fig. 6. These resistance values are for a martensitic condition except for carbon values too low to produce martensite on rapid cooling. Changes in carbon content affect the resistance of a martensitic structure much more than they do a pearlitic structure.

To calibrate the gage it is necessary to determine experimentally the relation between the equilibrium carbon content of plain carbon steel and ohms resistance of the gage wire after both have been heated in the same gas under standardized conditions.

EVALUATION OF CARBON PRESSURE

The general procedure used in the following experiments involved heating thin steel specimens in the atmosphere to be tested
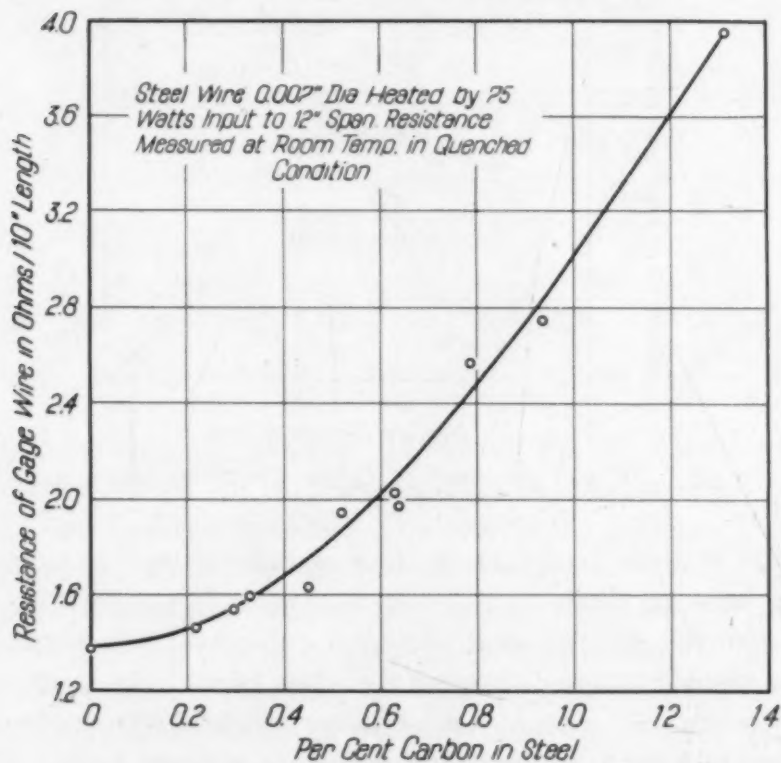
Fig. 7—Resistance of Carbon Gage Wire Versus Equilibrium
Carbon Content of Steel at 1700 Degrees Fahr.

until a carbon balance was attained; meanwhile some of this same gas was put through the hot wire gage and observations made of its effect on the wire resistance and expansion characteristics. The carbon content of the specimens after treatment was calculated from their change in weight; this was possible as they were kept bright

and clean so that weight changes represented equivalent change in carbon. In this way the relation between equilibrium carbon content of a steel heated to a given temperature in a given atmosphere and the resistance of the gage wire after exposure to this same gas can be determined.

Since the resistivity is a sensitive function of carbon content of the wire (Fig. 6) in the martensitic condition, and the carbon content is in turn a function of carbon pressure of the gas, then under standardized conditions the resistance of the wire can be used as a measure of gas carbon pressure.

Fig. 7 shows how the resistance of the gage wire after heating in endogas under standardized conditions varies with the equilibrium
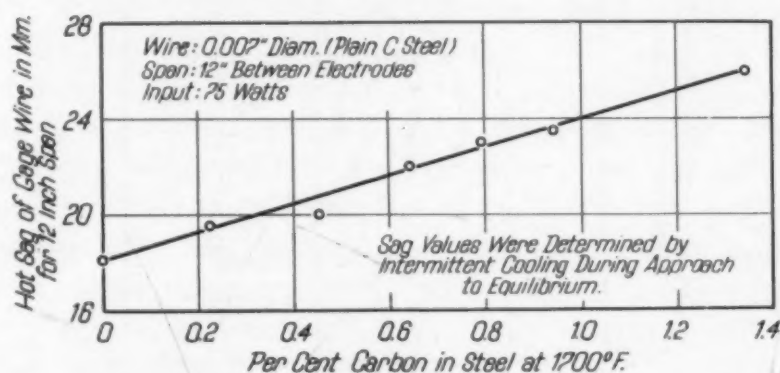
Fig. 8—Relation Between the Hot Sag of the Carbon Gage Wire in Endogas and the Carbon Content of Steel Heated to 1700 Degrees Fahr. in the Same Gas.

carbon content of the test specimens heated to 1700 degrees Fahr. (925 degrees Cent.) in this same gas. Similar curves can be determined for other temperatures in carbon ranges where single phase solid solution exists. The data in this paper all refer to plain carbon steel. Alloy steels will probably be subject to different carbon equilibria and different rates of reaction with the gas.

A comparison of the curves of Figs. 6 and 7 shows that the gage wire has a lower carbon content than the steel in the test furnace at 1700 degrees Fahr. (925 degrees Cent.). This is due to the fact that the wire was exposed to the gas at a temperature higher than 1700 degrees Fahr. (925 degrees Cent.) and therefore will absorb less carbon. The equilibrium carbon content of steel heated in a given gas varies inversely with temperature.

In these experiments the wire was heated to a constant arbitrary temperature between 1700 and 1800 degrees Fahr. (925 and 980

degrees Cent.) by applying a constant power input of 75 watts. Two primary considerations governed the choice of this temperature. First, the wire had to be heated above Ac_3 where it would be completely austenitic so that its equilibrium carbon content would be always determined by the carbon pressure of the gas. Second, the higher the temperature the more quickly this carbon equilibrium will
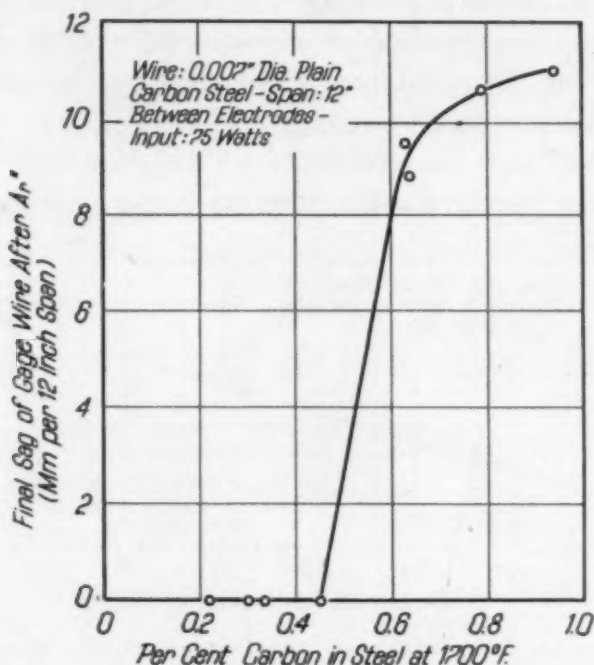
Fig. 9—Relation Between Final Sag of the Carbon Gage Wire After Heating and Quenching in Endogas and the Carbon Content of Steel Heated in the Same Gas to 1700 Degrees Fahr.

be attained. Changes in wire temperature due to variations in ambient temperature were considered to be negligible in the present experiments.

Changes in the amount of carbon in the gage wire visibly affected its physical behavior during heating and cooling. For example the total expansion of the wire at test temperature increased considerably with increasing carbon content. This effect is illustrated by the curve in Fig. 8 showing the relation between vertical hot sag of the wire and equilibrium carbon content of steel in the test furnace exposed to the same gas.

Another effect of carbon content on the behavior of the wire is in the temperature at which the martensitic transformation Ar'' occurs. When the carbon content is low the dilation occompanying

this transformation on cooling occurs at a relatively high temperature and is very rapid. As the carbon content of the wire is increased, the temperature at which the transformation begins decreases progressively and is apparent in the amount of sag in the wire. For example with a medium carbon content, the wire cools to tautness before the Ar" dilation begins and causes a momentary sag of several millimeters. After the dilation the wire continues to cool and shrink until it again becomes taut.

When the wire has a high carbon content it shrinks taut before the start of Ar"; the expansion during the transformation causes the wire to sag 11 millimeters and the temperature is then so close to ambient that no perceptible shrinkage occurs afterward.

Fig. 9 shows some observed values of the final sag in the gage wire plotted against the equilibrium carbon content of the steel specimens heated in the test furnace at 1700 degrees Fahr. (925 degrees Cent.). The fact that final sag of the wire is zero for carbon values below 0.45 per cent on the curve requires some comment. This is the point at which the dilation due to the martensitic transformation is just offset by the subsequent thermal contraction. For lower values of carbon this thermal contraction increases, due to higher temperature of the transformation, therefore the wire will have zero final sag for these carbon values, too.

The foregoing observations though offering an interesting commentary on the behavior of steel during hardening, are only incidental to the main objective of the hot wire gage. This objective is to measure quickly and reliably the essential characteristic of a combusted gas required for prevention of surface damage, namely its carbon pressure. By the means described here this is readily done and expressed in terms of the carbon content of any carbon or moderately alloyed steel which is in equilibrium with the atmosphere at a particular temperature.

With the information supplied by the hot wire gage, a gas generator can be set to provide the precise atmosphere required for protection of steel about to be charged in a furnace. Moreover the gas delivered and present in the furnace and actually in contact with the work can be checked as well to determine whether or not the generated gas is being delivered unimpaired to the work surface. Thus one of the most confusing factors responsible for great and unnecessary expense in manufacture can be brought under effective practical control.

Conclusions

For complete protection of a steel against changes in surface carbon during heat treatment, a protective gas must have a carbon pressure equal to that of the steel. Gas atmospheres capable of carbon pressure adjustment to suit all steels can be produced directly by thoroughly reacting mixtures of air and gas on a catalyst in a suitable generator. Carbon pressure of the gas can be controlled by regulating the air-gas feed ratio within narrow limits.

The amount of carbon absorbed by a fine steel wire heated to incandescence in an atmosphere can be used as a comparative measure of its carbon pressure for adjusting the atmosphere to balance the carbon in steels in a furnace at other temperatures.

DISCUSSION

Written Discussion: By Fred M. Reiter, formerly industrial gas engineer, The Dayton Power & Light Co., Dayton, Ohio, now major, Pittsburgh Chemical Warfare Procurement District.

With Mr. Gier's presentation, we pass another milestone in the journey toward complete understanding and control of atmospheric effects. His efforts are in the region least exploited—that of very low air to gas ratio (less than 30 per cent aeration)—the range that has come into greater usage with higher carbon steels, and about which less is known.

It has become increasingly important that equilibrium conditions be made more certain and quantitative, so as to avoid either carburization or decarburization. Innumerable data and conditions have been set up by many investigators, with varying analyses, citing CO to CO_2, H_2 to H_2O, and other ratios, to provide such equilibrium, until the heat treater is confused. In fact, each operator has set up individual ratios, indicated by flowmeters, pieces of wood, or other devices, to satisfy his own conditions, based upon his gas composition, furnace design, and other variables. This commentator suggested the use of raw gas, unmixed with any air, with controlled flow, to maintain "carbon pressures" of the atmosphere and the steel in equilibrium (*Metal Progress*, Sept. 1937). This set-up, however, has been extremely sensitive, and true equilibrium has been most difficult to maintain. Mr. Gier's gases seem quite sensitive, also, as from his Fig. 2 a very slight change in air to gas ratio, 2.55 to 2.85, apparently produces a great change in the equilibrium "carbon pressure", 0.2 to 1.3 per cent carbon.

It was our opinion, with the medium of raw natural gas, that the controlling factor of carburization and decarburization was the liberation of nascent atoms, C, H, O, Fe, and other elements involved, by the cracking or reformation of molecules of CH_4, CO_2, CO, H_2O, etc., on the surface of the steel. Gaseous oxides are practically nil in raw dry natural gas. We found that "carbon pressures" could be increased by supplying more gas molecules to crack, or by controlling the rate of gas flow. Increased tempera-

tures accelerated such atomic changes, so that fewer total molecules need be provided at higher temperatures. Mr. Gier's Fig. 4 indicates a similar high temperature acceleration and carbon pressure effect.

In Mr. Gier's work, utilizing an external cracker or reaction chamber, assuming a constant reformed gas flow, the appreciable variable as indicated in Table I seems to be moisture, whose variation from 1.80 per cent to 0.13 per cent produces a corresponding change in equilibrium "carbon pressure" in the steel from 0.20 to 1.34 per cent carbon. Are we to infer that H_2O is the control gas? Fig. 3 emphasizes the moisture effect by relating dew point to "carbon pressure" values. In other words, has the control mechanism been taken away from the CO and CO_2 percentages, and would similar "carbon pressures" be developed in the dehydrated reformed gas? It may be that each of the many gases developed for equilibrium conditions has a different mechanism and preponderant control factor. This is interesting. Mr. Gier's work is excellently quantitative and provides definite procedures and expectations for his gas, which is of immense practical value to the furnace operator.

The big question in my mind is whether such balanced "carbon pressures" are readily reproducible in different localities with different gases, different conditions of furnaces and operators, particularly in tool hardening, where each charge may be different.

One answer is the "hot wire gage" as presented by Mr. Gier. Here is a genuine contribution. We trust that this device will be available to the industry as a direct and simple measurement of "carbon pressure". Mr. Gier has opened a new vista in quantitative atmosphere control, leading toward predictability and universality.

Written Discussion: By E. K. Spring, metallurgist, Henry Disston & Sons, Inc., Philadelphia.

This paper, by Mr. Gier, follows one on the same subject presented in 1939 of which the author was co-producer. In the present paper the protective gas differs from that of a year ago, in that it is capable of being produced in either a carburizing or decarburizing condition and must be controlled as to which of these qualities is in the ascendency.

The "carbon pressure" theory advanced as an explanation of probability of carburizing by the gas is sound and analogous to the partial pressure theory of gases. The evaluation of this "carbon pressure" by means of the "hot wire gage" is perhaps the more important part of the paper. Is it safe to assume that by means of this gage the proper gas can be developed for most, if not all, analyses of steel? I have been privileged to examine a small number of mildly alloyed steels of types quite prone to decarburization, which had been treated in "endogas", and found the surface and sub-surface condition excellent. Whether or not this would hold for those forms of high speed steel which are most prone to decarburize should be an interesting point which I hope may be covered at another time.

The ability to treat without decarburization is an enormous advantage in three ways. The utmost capabilities of tools can be brought out in no other way; losses are reduced; costs of finishing operations applied after treatment may be reduced.

Such work as this paper represents, pointing, as it does, a way to get away from messy salts and packing of tools, is certainly a big step in the right direction. Heat treaters should be more appreciative of this type of information.

Written Discussion: By Edward E. Slowter, chemical engineer, Battelle Memorial Institute, Columbus, Ohio.

Mr. Gier's paper makes a valuable addition to information on controlled atmosphere equilibria. The hot wire gage which he describes appears to be a simple and flexible instrument for the measurement of one of the important properties of a controlled atmosphere, i.e., its behavior towards carbon in steel. The need for such an instrument has long been felt, particularly by the small and intermittent users of controlled atmospheres. It is to be hoped that this device which Mr. Gier has described can be developed into a cheap, compact unit which will be commercially available.

The following points are offered to help explain some specific phenomena noted in this paper:

1. In commenting upon the carbon equilibria (or carbon pressure) of atmospheres produced by a constant air-gas mixture at various formation temperatures, Mr. Gier states (page 676), "The reason for the upturn in the curve (Fig. 4) above 1800 degrees Fahr. (980 degrees Cent.) is not yet understood." This curve shows that as the atmosphere formation temperature increases above 1800 degrees Fahr. (980 degrees Cent.) its carbon pressure increases quite rapidly—i.e., the atmosphere rapidly comes into equilibrium with higher carbon steels. It is suggested that this is due to the reactions which cause the removal of CO_2 and H_2O being driven nearer completion. If Mr. Gier's Fig. 3 is replotted so that the water content is given as mm. pressure instead of dew point, it will be seen that as the water content of the atmosphere is decreased the carbon pressure of the atmosphere increases very rapidly and in a nonlinear fashion. It is believed that CO_2 reacts in a similar manner. Now as the formation temperature of the atmospheres described by Mr. Gier is increased, the amounts of CO_2 and H_2O present in the atmosphere decrease, and as they reach the lower values the carbon pressure of the atmosphere increases more rapidly, since, as shown by Mr. Gier and others, the carbon pressure does not vary linearly with the H_2O and CO_2 contents. In addition, the fact that the equilibrium amounts of CO_2 and H_2O do not vary linearly with temperature may also intensify the effect noted by Mr. Gier, but at 1800 degrees Fahr. (980 degrees Cent.) it is doubtful that these reactions have reached the knees of their respective equilibrium curves.

2. On page 681 it is pointed out that curves 6 and 7 show that the gage wire consistently contained less carbon when in equilibrium with a given atmosphere than a steel in equilibrium with the same atmosphere. Mr. Gier suggests that the difference was caused by the fact that the steel was heated to only 1700 degrees Fahr., while the wire was heated to 1700 to 1800 degrees Fahr. (925 to 980 degrees Cent.). This would indicate that the temperature difference between the wire and the steel did not exceed 100 degrees Fahr., which is not a large differential in view of the considerable difference between their behaviors. It is suggested that the wire may have been hotter

than 1700 to 1800 degrees Fahr. (925 to 980 degrees Cent.) because of the difficulty of obtaining a true measure of the wire temperature. Mr. Gier does not state how the temperature of the wire was determined but it was probably measured by optical means. In work done at Battelle Memorial Institute it was found to be extremely difficult to determine the temperature of a single wire heated internally in an atmosphere which kept the surface of the wire bright. Under these conditions the emissivity of the wire is variable but is never close to true black body conditions, and the actual temperature of the wire is always hotter than the temperature read by optical instruments. Therefore, the wire used in Mr. Gier's experiments may have been considerably hotter than 1800 degrees Fahr. (980 degrees Cent.) if optical measurements were used.

Written Discussion: By R. P. Koehring, metallurgist, Moraine Products Division, General Motors Corp., Dayton, O.

Because of the increasing interest and importance of the subject of suitable media in which to heat metals without surface or chemical changes, the paper by Mr. Gier is of especial interest.

Controlled atmosphere generators have been in use for some time to produce special atmospheres which will prevent metals from oxidizing when heated. The question of carbon equilibrium between a gas and an iron-carbon alloy is still another question and the author deserves commendation for the work he has presented here, which describes his work of producing in commercial equipment a gas which can be controlled so that it will be in equilibrium with the carbon in steel over the whole usual range of iron-carbon alloys.

Curves have previously been published showing, in terms of ratios of CO to CO_2 and water vapor to hydrogen, the point at which oxidation or reduction and carburization or decarburization occur. These curves have been very interesting but their interpretation in terms of commercially prepared gases have been difficult.

Mr. Gier has presented data to show the conditions for carburization or decarburization as a function of the air-gas ratio of a commercially available gas generator. It is certainly interesting to note that to vary the conditions of equilibrium of a gas with steel containing from 0.2 to 1.4 per cent carbon requires but a change in air-gas ratio of 2.5 to 2.9. This brings to mind problems of more accurate metering and control of gas generators to produce gas for special heat treating or sintering operations which will remain within these narrow ratio limits.

This subject is of particular interest to those engaged in powder metallurgy, especially powder metallurgy of iron. Here, due to the very large surface of parts pressed from iron powder, the effect of carburization and decarburization is of great importance.

In the manufacture of parts from iron by powder metallurgy, the sintering operation is usually done at temperatures above those mentioned in Mr. Gier's paper. Also compositions of iron and carbon are of interest with carbon contents below those mentioned. It is hoped that Mr. Gier will be able to extend his investigations to cover these conditions.

It can readily be seen that present gas composition indicating devices can-

not indicate carbon pressure. The hot wire carbon gage, though perhaps not perfected, is a very interesting start to develop such an instrument, and it would be desirable to have such an instrument continuously indicating and recording.

Written Discussion: By Sam Tour, consultant, C. I. Hayes, Inc., Providence, R. I.

Mr. Gier is to be complimented upon that portion of his paper which has to do with the development of his new device which he calls "a hot wire gage" for evaluating the carburizing tendencies of a furnace atmosphere. The following discussion is directed to the first portion of his paper which is devoted to atmosphere generation.

The reaction between one volume of natural gas and two or more volumes of air is definitely an exothermic reaction. This situation is fully explored in the paper on "Furnace Atmosphere Generation" presented by the writer at this 22nd Annual Convention of the American Society for Metals. Since the fundamental reactions are exothermic, not endothermic, the basic assumptions upon which the term "endogas" was coined are erroneous and the term "endogas" is misleading.

In Table I are listed what is described as "Several typical endogas analyses". The ratio of nitrogen to hydrogen and carbon monoxide in these analyses shows that they could have been produced only from a ratio of approximately two of air to one of gas (methane). This is peculiar, in view of the fact that Fig. 2 calls for air-gas ratios between 2.57 to 1 and 2.87 to 1 for equilibrium with steels of the same carbon content as referred to in Table I.

The readily apparent relationship between the columns of figures shown in Table I is between the water vapor content and the per cent carbon content. It will be noted that in these two columns the carbon in the steels is inversely proportional to the moisture in the atmosphere.

Although Mr. Gier ascribes the carburizing or decarburizing effect to the relationship between CO and CO_2, he reports an analysis of zero CO_2. The effect of methane (CH_4) and hydrogen on the carburizing and decarburizing action must be considered. Table I shows both of these present. Sykes and Pring and Fairlee have determined the relationship between methane and hydrogen on the decarburizing and carburizing reactions. Their curves have been reproduced in the paper "Water Vapor in Furnace Atmospheres" being presented by the writer at this Convention and printed in this issue of TRANSACTIONS, page 693. For neutrality to carbon in steel, the ratio of methane to hydrogen varies with the carbon content of the steel. The analyses given by Mr. Gier in Table I are in conformance with the results of Sykes, with the one exception of the first gas which, incidentally, is high in water vapor.

Not only do we have insufficient knowledge to conclude that carbon monoxide is the one and only carbon carrier, but we have knowledge to the effect that methane is an important constituent in connection with carburization and decarburization of steel.

Mr. Gier makes the statement that his gas generator unit "requires no further processing such as removing CO_2 and water vapor", yet he gives

analyses of products of combustion which are not in accordance with the accepted equilibrium constants for the combustion reaction. Mr. Gier makes the statement, "The process is endothermic and will not proceed to equilibrium unless the catalytic action is completely effective". This statement infers that endothermic reactions require a catalyst in order to proceed to equilibrium. This is not in accordance with the accepted ideas of those who have studied reactions of all types. Whether a reaction does or does not proceed to equilibrium is not related to whether the reaction is endothermic or exothermic. However, it is well to repeat that the reactions referred to by Mr. Gier are in themselves exothermic.

The data plotted in Fig. 2 are at variance with the data obtained in Table I and inconsistent with the statements made in connection with Fig. 3: "This curve applies only to a gas mixture of 20 per cent CO, 40 per cent H_2 and 40 per cent N_2". If it were true, and it is doubted, that the gas generator referred to is able to burn a mixture of air and gas without the formation of carbon dioxide or water, the products of the air-gas feed ratios shown in Fig. 2 would contain from 44.2 to 47.4 per cent of nitrogen. Table I calls for a nitrogen content of 39.9 to a maximum of 43.5 per cent. These could not be obtained from the air-gas ratios shown in Fig. 2 if the generator actually operated in the manner described.

In Fig. 4, Mr. Gier attempts to show the variations in activity towards steel due to variations in generator temperature for a constant feed ratio of air to gas. He fails to state what feed ratio was used in these experiments. Having done this for one air-gas ratio, an attempt is made to generalize and state that it applies to various air-gas ratios. The correct interpretation of this one curve would be that for the given air-gas ratio, whatever it may have been, the generator temperature must be maintained between 1700 and 1800 degrees Fahr. (925 and 980 degrees Cent.) in order to produce an atmosphere suitable for a 0.50 per cent carbon steel at 1700 degrees Fahr. (925 degrees Cent.). The data contained in Fig. 4 cannot be stretched to cover any other air-gas ratio or any other temperature range.

Assuming, for the moment, but not granting, that the air-gas feed ratios shown in Fig. 2 are correct, we can consider the statement made that—"This gas is inherently capable of adjustment to chemical balance with steel of any carbon content by simply regulating the feed ratio within narrow limits". Whether or not this is true is dependent upon the definition of the term "inherently capable of adjustment". The range of air-gas ratio shown in Fig. 2 calls for controlling the percentage of gas admitted to the air-gas mix to an extent which is beyond the sensitivity of the usual proportioning mixtures. A gas-air mix containing precisely 25 per cent of gas is needed for a 0.2 per cent carbon steel, a mix containing precisely 27 per cent of gas is needed for a 0.50 per cent carbon steel, and a mix containing precisely 28 per cent of gas is needed for a 1.3 per cent carbon steel. This fine micrometer control of percentage of gas admitted to the gas-air mixture is difficult to obtain. A system requiring such micrometer control is hardly to be called one "inherently capable of adjustment".

Although Mr. Gier has not given the analyses of the products of com-

bustion from operating his generator at various temperatures, the writer undertakes to predict that the main variation due to the temperature change will be along the lines indicated in the writer's paper, published in this issue of TRANSACTIONS, page 693.

Written Discussion: By Norman E. Woldman, chief metallurgical engineer, Bendix Aviation Corp., Bendix, N. J.

Mr. Gier's paper, discussing his development of a balanced protective atmosphere for the hardening of carbon and alloy steels without subsequent carburization or decarburization, is an excellent contribution to our ever increasing knowledge of clean-hardening. The fact that his process has been put successfully into commercial practice warrants hearty thanks and appreciation from the industrial heat treaters.

Controlled atmosphere furnaces, to be successful for the hardening of steel parts, must meet the following three requirements:

(1) Produce no decarburization.
(2) Produce no carburization.
(3) Produce no scale.

In our aircraft plant we have experienced the usual troubles with scale on the hardened steel surfaces, which scale has to be removed electrolytically by the Bullard-Dunn Descaling process. Scale formation means loss of iron in addition to the decarburization. For certain aircraft parts, which cannot be ground after hardening and where the dimensions are to be held within very close tolerances, scale formation can be quite serious.

We have recently installed a large continuous hardening furnace utilizing Mr. Gier's endogas process, and the results have been very satisfactory.

Since our highly stressed parts are made from S.A.E. 3135, S.A.E. 4640, S.A.E. 3250, S.A.E. 4350 and S.A.E. 6150 steels, we have experimented to establish one gas-air ratio for the generator, which mixture could be used successfully with all the above steels. This we found to be as follows:

Volume of gas (manufactured city gas) .... 200 cubic feet per hour
Air .... 150 cubic feet per hour

This periodic gas analysis of the atmosphere in the hardening furnace showed 3.0 to 4.0 per cent CO_2, 15.5 to 22.0 per cent CO, 0.02 to 0.50 per cent O_2, 5.0 to 7.0 per cent CH_4, 26.0 to 30.0 per cent H_2 and 39.0 to 42.0 per cent N_2. The generator is maintained at a temperature of 1850 degrees Fahr. (1010 degrees Cent.). The furnace temperature is adjusted to the proper hardening temperature for the particular alloy steel being oil-hardened. All our work passing through the furnace has been scale-free and clean, although it did have a light gray color. Periodic micro-examination and hardness testing of the surfaces of the hardened parts showed no evidence of either carburization or decarburization.

However, there is one drawback to this endogas process, and that is the soot deposit in the generator. This necessitates periodic burning out of this soot with subsequent shut-down of the furnace. At present we operate the generator and furnace continuously for 40 hours, then drop the temperature of the generator from 1850 to 1350 degrees Fahr. (1010 to 730 degrees Cent.) and blow air through the generator for 16 hours. When the soot in the gen-

erator is burned out and the temperature of the generator is brought back to 1850 degrees Fahr. (1010 degrees Cent.), the furnace has to be purged for at least one hour before production parts can be put through the furnace again for hardening. To eliminate this production shut-down, we found it necessary to use two gas generators for the furnace so that one generator can be operating while the other generator is being cleaned of soot.

We would like to see Mr. Gier continue his experimental work with this endogas in the direction toward eliminating the soot deposition in the generator.

Oral Discussion

F. M. Reiter:[1] I wonder if I could make one remark on the discussion of endothermy and exothermy in the reformation of gas with air in external gas generators, in defense of Mr. Gier. I want to say, regardless of what the theoretical considerations might be, we have been unable to maintain continuous combustion in such generators utilizing natural gas and air in ratios below 4 of air to 1 of gas. Anything below this ratio we must supply heat externally, due possibly to radiation from the reaction chamber or other heat losses. Below this ratio, 4 to 1, from the practical viewpoint, the reaction is undoubtedly endothermic.

Author's Reply

To answer Mr. Reiter's question regarding the effect of dew point on "endogas" carbon pressure, I think water vapor may be considered as governed by the law of mass action the same as the other reacting components. If endogas were dried completely, there would on reheating be more water formed by H_2 reacting with CO_2; this would have the effect of increasing the carbon pressure. In practice no drying is required as the moisture present in the gas is only the small amount that is necessary for chemical balance.

As to the reproducibility of endogas carbon pressures with various types of fuel, our experience shows that natural gas is preferable in our present type of generator, but several different city gas compositions have been used successfully. Theoretically any fuel gas should be suitable for making endogas, providing it is correctly proportioned with air and the mixture thoroughly reacted.

The relatively high CO_2 and CH_4 values reported by Dr. Woldman indicate an excessively rich mixture that is not being completely reacted. This high residual CH_4 content could cause sooting. In the laboratory we have run a generator continuously for several weeks producing high carbon pressure gas without soot clogging, but there the mixture was thoroughly reacted and the product gas contained less than 1 per cent CH_4.

In preparing the endogas compositions described in this paper, we have simply carried out an old process to an unusual degree of completeness. The result is new and useful because it consists of an equilibrium gas mixture whose carbon pressure can be readily and accurately adjusted.

Commenting on Mr. Tour's remarks about catalysts in gaseous reactions,

[1]See page 684 for Mr. Reiter's business association.

I agree that catalysts do not determine what equilibrium one gets, but they certainly may determine in practice whether one gets it. It was only with the aid of an effective catalyst that the thorough reactions denoted by the gas composition of Table I could be obtained.

The fuel ratio range is narrow, admittedly, but I believe that it is well within the practical range of control for short cycle heating at least. As to the actual numerical values of the air-fuel ratio, that of course would depend upon the exact composition of fuel gas. Mr. Tour's question regarding the air-gas ratios of Fig. 2 has no point since the fuel gas used was Pittsburgh natural gas as reported, and not pure methane as he assumed it to be.

A mutual equilibrium of the gas components, meaning a practical equilibrium, is necessary for control of carbon pressure with any precision by varying the air-gas ratio. As Mr. Reiter pointed out, published data on the reaction of air-gas mixtures seem to vary widely in their composition. This I would explain as being due to incompleteness of the reactions obtained.

Referring to the amount of CO_2 shown in the table for the carbon steels of medium and higher value, I do not mean to imply that there was no CO_2 present; what I mean to say is that the Orsat analysis, which is only accurate to 0.1 per cent, did not reveal CO_2. Therefore, I gave it as zero per cent, without attempting to say how much was in the hundredths place.

Undoubtedly the methane or hydrocarbon content of the gas does have an effect on the carbon pressure of the gas. However, since we presumably are dealing with an equilibrium gas, we may consider the hydrocarbon as having an indirect effect upon the carbon pressure by its effect on the CO and CO_2 content.

To simplify the consideration of this, in dealing with the carbon pressure we can take the CO and CO_2 values as indicative of carbon pressure. However, in these tests we were primarily concerned with the effect of the gas rather than its actual analysis; this is true of protective atmospheres in general. The utility of the hot wire gage comes from the fact that it only responds to the effect of the gas on the steel rather than to some particular physical characteristic of the gas not related to carbon pressure.

Mr. Koehring mentioned the desirability of tests of higher and lower temperature. We have made some such tests on sintered compacts and we find that there is a systematic relationship between air-gas ratio, dew point, and carbon content for the higher temperatures. However, the relationship is different for different temperatures.

FURNACE ATMOSPHERE GENERATION

By Sam Tour

Abstract

In burning rich mixtures of fuel gas and air, the composition of the products of combustion from a given ratio of gas to air are found to be dependent upon the temperature of the combustion chamber. At low combustion chamber temperatures heavy soot deposits result and the gaseous products of combustion are low in hydrogen and carbon monoxide and high in water and volatile hydrocarbons. At high combustion chamber temperatures coke deposits result and the gaseous products of combustion are high in hydrogen and carbon monoxide and low in water vapor. Very seldom are the reactions truly endothermic. They are usually true exothermic combustion reactions. An intermediate temperature range of 1600 to 1900 degrees Fahr. may be used where difficulties due to heavy soot or heavy coke do not develop. This range is wide enough to allow for a considerable variation in the gaseous products of combustion. Temperature control within this range gives uniform performance. Numerous methods of obtaining this temperature are described.

METALLURGISTS are fully aware of the importance of temperature. The temperature of the furnace chamber in which the metal is being heated is determined by the metal and the results desired from the heating of the metal. Obviously the atmosphere gases in the furnace surrounding the metal must be heated to the same temperature required by the metal itself. The literature abounds with equilibrium curves showing the various ratios of gases in equilibrium at various temperatures. These equilibrium curves have to do with the reactions which take place between the gases themselves and also the reactions which take place between the gases and the metals. The literature also contains a number of curves showing the products of combustion of various mixtures of air and gas. These curves represent the volume percentages of products of combustion from various air-gas ratios. In an article published in 1932,[1] the present author presented a typical set of curves showing carbon

dioxide, carbon monoxide and oxygen present for various ratios of air to gas at 2400 degrees Fahr. (1315 degrees Cent.). Since that time, a number of authors have published similar curves but have failed to state the temperatures for which these curves apply. There has been a tendency to assume that the products of combustion of a given mixture of gas and air are entirely dependent upon the ratio of gas to air introduced into the combustion chamber and thus are independent of the temperature of the combustion chamber.

A large percentage of the controlled atmospheres required for the heat treatment of steel are those obtained as the result of burning rich mixtures of gas and air. By a rich mixture is meant a mixture in which the amount of air supplied is insufficient for complete combustion of the gas. This is often referred to as "partial combustion" with a deficiency of air. It is in this field that combustion chamber temperatures play their most important role.

EFFECT OF COMBUSTION CHAMBER TEMPERATURES

Burning city gas and air in the ratios of 1 of air to 1 of gas and 2 of air to 1 of gas, and maintaining combustion chamber temperatures at various points from 1200 to 2200 degrees Fahr. (650 to 1205 degrees Cent.), and making the usual analyses of the products of combustion, the effect of changes in the temperature of the combustion chamber becomes very apparent. The results are shown in Fig. 1. It will be noted that as the temperature of the combustion chamber is increased, the products of combustion for the same air to gas ratio contain less illuminants, slightly less carbon dioxide, considerably more carbon monoxide and greatly increased quantities of hydrogen. Unfortunately, when this work was done, no direct determinations of water vapor content were made. Due to the large quantities of residual illuminants present in the products of combustion and due to the large quantity of soot and carbon formed in burning these rich mixtures at the lower temperatures, it is impossible to calculate the volume relationship between the initial gases and the products of combustion. It is, therefore, impossible to arrive at a logical basis for the calculation of water vapor content of the products of combustion. Experience shows that the water vapor content decreases as the temperature of the combustion chamber increases.

Burning a mixture of propane gas (C_3H_8) and air and maintaining the combustion chamber at various temperatures, and using

an air-gas ratio of 8 of air to 1 of gas, the average analyses of the products of combustion are shown in Fig. 2.   Here it is seen that the hydrogen content of the products of combustion increases continuously and rapidly as the temperature of the combustion chamber is
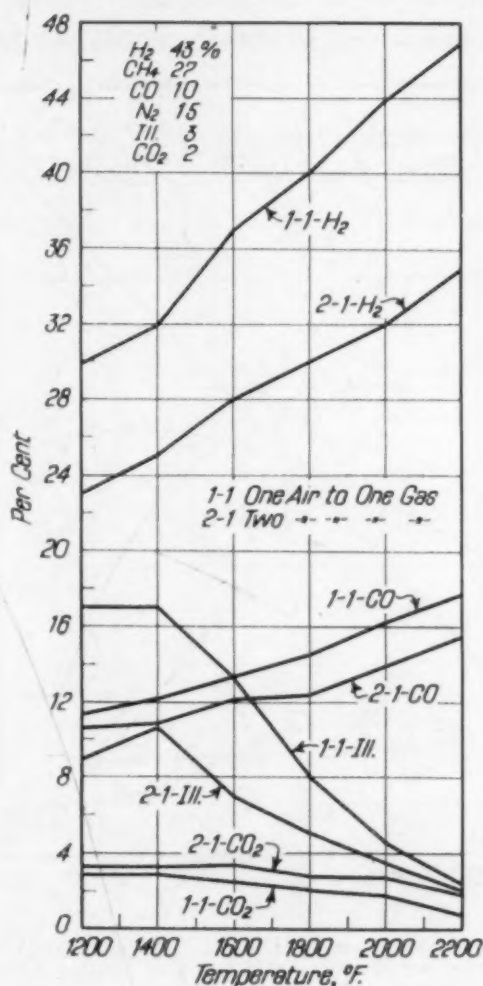

Fig. 1—Effect of Changes in Temperature of Combustion Chamber.   City Gas.

increased.   The percentage of carbon monoxide in the products of combustion increases to a combustion chamber temperature of around 2000 degrees Fahr. (1095 degrees Cent.) and then decreases.   This phenomena will be referred to later.   Illuminants and carbon dioxide both tend to decrease as the combustion chamber temperature increases.

In the combustion of propane gas, we have a base material of known composition and, within certain limits, we can calculate the

amount of water vapor present in the products of combustion. The calculation is based on the assumption that for each volume of propane gas which is burned, there will be produced three volumes of carbon monoxide plus carbon dioxide gases, and four volumes of hydrogen plus water vapor. To the extent that carbon is lost in the formation of illuminants and in the formation of tar, soot and pitch,
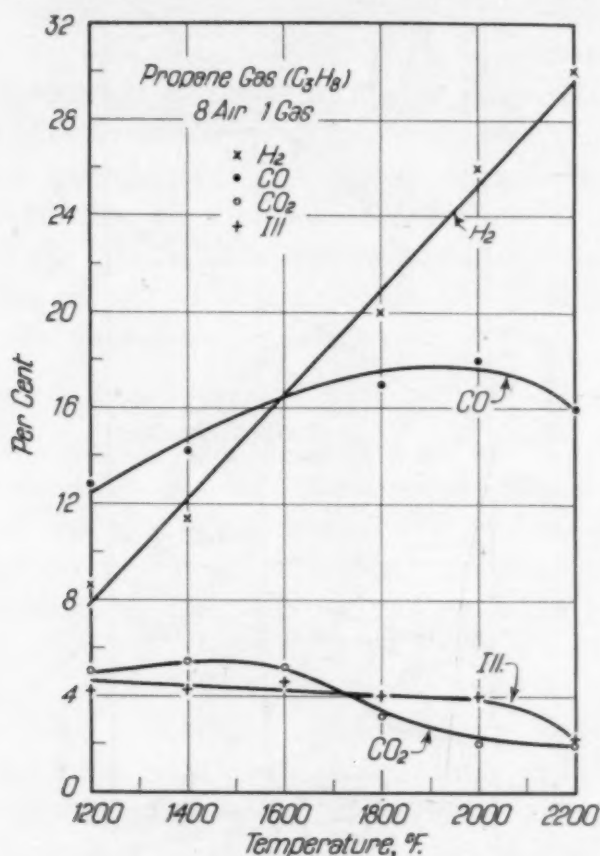
Fig. 2—Effect of Changes in Temperature of Combustion Chamber. Propane Gas (C₃H₈). Average Curves.

the calculated water vapor will be less than the true water vapor content of the products of combustion. The results shown in Fig. 2 revised and corrected for water vapor content are shown in Fig. 3. Here the fact that the water vapor content of the products of combustion decreases rapidly as the temperature of the combustion chamber is increased becomes quite evident.

The decrease in carbon monoxide content at temperatures above 2000 degrees Fahr. (1095 degrees Cent.) is due to the large loss of carbon in the form of coke and carbon particles and heavy oils of the naphthalene type. In many instances, the atmosphere desired

from an atmosphere generator is one which requires even richer mixtures than the 8 of air to 1 of propane gas covered by the curves in Figs. 2 and 3. With these still richer mixtures, the problem of coke deposition in a combustion chamber operating at 2000 degrees Fahr. (1095 degrees Cent.) or higher becomes even more accentuated. Continued burning of excessively rich propane gas and air mixtures
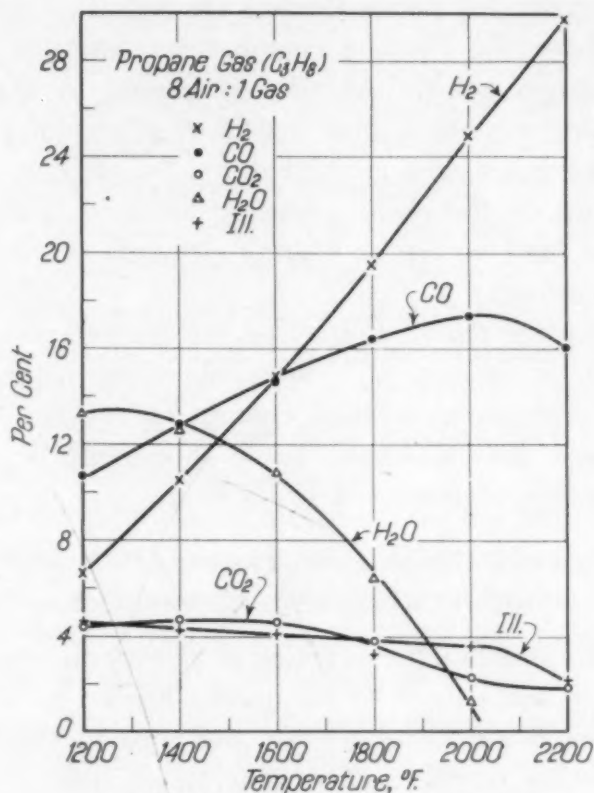
Fig. 3—Effect of Changes in Temperature of Combustion Chamber. Propane Gas (C_3H_8) 8 air : 1 gas. Corrected for H_2O.

in a combustion chamber at high temperatures results in loading the combustion chamber with coke and the outlet pipes with tar and naphthalenes.

At low combustion chamber temperatures, the gases are not broken down so completely as to form heavy coke or pitch deposits, but form large quantities of so-called "illuminants", light oil vapors and soot. The gases coming from the combustion chamber, when it is operated at too low a temperature, are usually referred to as "smoky". The soot and oil vapors which are carried along rapidly foul the furnace and the work in the furnace. If cooling or cleaning equipment is used to dehydrate the products of combustion, the pas-

sageways become coated with soot. Some of the oil vapors are condensed and removed with the condensed water vapor.

Furnace atmosphere gases carrying large quantities of soot and large quantities of oil vapors are particularly objectionable in metallic resistor heated electric furnaces where the gases come in contact with the heating elements. When the current is on, the heating elements in an electric metallic resistance furnace are operating at temperatures considerably above the furnace chamber temperature or the work temperature control point. As the oil vapors in the atmosphere strike the heating elements, they are cracked to form carbon plus lighter vapors or gases such as methane and hydrogen. The carbon residue builds up on the electric heating elements. Within a short time, the carbon built up on the heating elements may be sufficient to cause short circuiting.

It seems evident that a control of the temperature of the combustion chamber is necessary. The combustion chamber should be maintained at a temperature high enough to prevent the excessive formation of soot and oil vapors, but it should not be so high as to cause the formation of coke and heavy tars.

PRODUCTS FROM LOW TEMPERATURE AND HIGH TEMPERATURE COMBUSTION

In many installations the practice is to generate the furnace atmosphere in a separate piece of equipment known as a "generator", to cool the gases from this generator and then to reintroduce them into a heat treating furnace. The general situation with regard to the effect of combustion chamber temperature on the operation of this type of equipment is shown in the following tabulation:

	Too Low Temperature	Too High Temperature
Direct Products from Combustion Chamber:	High Water Vapor. Low Hydrogen. Medium CO_2. Medium CO. High in Light Oils. Low in Heavy Oils. High in Soot.	Low Water Vapor. High Hydrogen. Lower CO_2. Higher CO. Low in Light Oils. Higher in Heavy Oils. High in Coke.
Condensate in Coolers:	High in Water. Low in Heavy Oils. High in Soot.	Low in Water. High in Tar & Naphthalenes. High in Coke Particles.
Reactions on Reheating:	Excessive Cracking of Light Oils. Excessive Carbon Deposition. Smoky Atmospheres.	Slight Cracking of Light Oils. Slight Cracking of Methane. Decarburizing Atmospheres.

Exothermic Versus Endothermic Reaction

Combustion engineers are well acquainted with the significance of the term "limit of inflammability" as applied to the various gaseous fuels. Mixtures of gas and air of such proportions as to be outside of the limits of inflammability will not continue to burn when ignited. Combustion engineers are also acquainted with the term "ignition temperature". The ignition temperature as applied to gaseous fuels is the temperature to which the gas and air mixture must be heated in order that combustion begin. If the amount of heat liberated by the combustion is sufficient to raise the temperature of the surrounding gas-air mix to the ignition temperature, then combustion will continue of itself. Thus the limit of inflammability of a gas-air mixture is really dependent upon the initial temperature of that gas-air mixture as well as upon the ratio of gas to air. As the temperature of the gas-air mix is raised, the limits of inflammability become broader. If the entire mixture of gas and air is raised to a temperature equal to or above the ignition temperature, then the term "limits of inflammability" has no significance.

Any reaction which is accompanied by the liberation of heat is an exothermic reaction. Any reaction which takes place and is accompanied by an absorption of heat is an endothermic reaction. In determining whether a reaction results in the liberation or the absorption of heat, we must consider the energy content of the initial constituents of the reaction at some given temperature and the energy content of the products of the reaction at that same temperature. If the total energy content of the products of a reaction is less than the total energy content of the constituents that entered into that reaction, then some heat was liberated in the reaction and the reaction was exothermic. On the contrary, if the products of the reaction contain more energy than the raw constituents entering into the reaction, then some heat must have been absorbed and the reaction was endothermic. By "energy" of a gas is meant the heat of formation of the gas and not its sensible heat in the form of temperature. As stated before, the energy content must be considered for both the reacting constituents and the products when they are at the same temperature. This will eliminate the complication of heat absorption or liberation in the form of changes in temperature.

In the furnace atmosphere field, we are concerned with a number of known gases, such as hydrogen, oxygen, carbon monoxide, carbon

dioxide, water vapor, methane, propane and nitrogen. Fortunately, we know the heats of formation or energy content of each of these gases. Therefore, it is possible to calculate the total energy content of the gas-air mixture being supplied to a furnace atmosphere generator and the total energy content of the products of combustion coming from it. By this method of calculation, it can be shown that, even with such rich gas-air mixtures as to require the addition of considerable heat to the combustion chamber to maintain the reaction, the reactions taking place in the combustion chamber of furnace atmosphere gas generators are still exothermic.

In the cases of simple constituent gases, such as methane or propane, the question of whether the reaction was exothermic or endothermic is simple to calculate. The methane or propane is broken down into its constituents carbon and hydrogen. This breaking down absorbs a known amount of energy and releases a given ratio of hydrogen to carbon. The heats of formation of the products of the combustion are known. With this data and with an analysis of the products of combustion as to hydrogen, water vapor, carbon monoxide and carbon dioxide content, the energy balance is determinable by use of the following data:

For Methane:

Energy of formation of methane—18.5 KC

From each equivalent volume of methane two volumes of hydrogen are produced and, therefore, 9.25 KC were absorbed per volume of hydrogen produced.

For each equivalent volume of carbon monoxide in the products of combustion 26.4 KC were liberated.

For each equivalent volume of carbon dioxide in the products of combustion 94.4 KC were liberated.

For each equivalent of water vapor in the products of combustion 57.8 KC were liberated and 9.25 absorbed in the formation of the hydrogen leaving a net liberation of 48.55 for each equivalent of water vapor, H_2O.

For Propane:

Energy of formation of propane (C_3H_8)—24.75 KC

From each equivalent volume of propane four equivalents of hydrogen (H_2) and, therefore, 6.2 KC were absorbed per volume of hydrogen produced.

For each equivalent volume of carbon monoxide 26.4 KC were liberated.

For each equivalent volume of carbon dioxide 94.4 KC were liberated.

For each equivalent volume of water vapor in the products of combustion 57.8 KC were liberated and 6.2 absorbed leaving a net liberation of 51.2 KC for each equivalent of water vapor, H_2O.

It is assumed that all of the gases in the products of combustion follow the ideal gas laws sufficiently close that changes in the volume per gram molecule of gas with changes in temperature are substantially the same. These data have been applied for each of the analyses shown for the different temperatures in Fig. 3 for the combustion of propane gas. Even at the high temperature of 2200 degrees Fahr. (1205 degrees Cent.) where the moisture is practically zero and the carbon dioxide is only 2 per cent and the hydrogen is near 30 per cent, the reaction is definitely exothermic. As the combustion chamber temperatures are lowered, the combustion reaction for the mixture of 8 of air to 1 of propane gas becomes still more exothermic because the products of combustion contain considerable water vapor and much less hydrogen. This same method of calculating applied to the combustion of methane with gas-air ratios of 5 of air to 1 of gas proves that the reaction is decidedly exothermic.

In spite of the fact that practically all furnace atmosphere generators operate with gas-air mixtures which react exothermically, it is still necessary to supply external heat to the combustion chamber if satisfactory combustion is to take place and if the products of combustion are to be controlled. Temperature control of the combustion chamber is just as necessary, although possibly not to such small or narrow temperature limits or ranges, as is temperature control in the heat treatment and annealing of metals.

Temperature Range for Combustion Chamber

A description has been given of the operating difficulties which develop if very rich gas-air mixtures are burned in combustion chambers whose temperatures are either excessively low or excessively high. It has been shown that the products of combustion vary in composition as the combustion chamber temperature is changed. If a uniform product of combustion is to be obtained, a uniform combustion chamber temperature must be maintained as well as a supply of a uniform gas and air mix.

In burning city gas, natural gas, or propane gas, a combustion chamber temperature maintained above 1600 degrees Fahr. (870 degrees Cent.) will eliminate most of the operating difficulties due to low temperatures and a combustion chamber temperature below 1900 to 2000 degrees Fahr. (1040 to 1095 degrees Cent.) will eliminate most of the operating difficulties due to high temperatures. The

particular and best temperature of operation between 1600 and 1900 degrees Fahr. (870 and 1040 degrees Cent.) must be determined by the needs as to composition of the product coming from the generator. If higher hydrogen is desired, the higher operating temperatures should be used. If lower hydrogen is desired, the lower operating temperatures should be used. If the products of combustion are to be cooled so as to remove surplus moisture before they are introduced into a furnace for atmosphere purposes, the question of water vapor content of the products of combustion as they leave the generator is not of great importance. If the gases are not to be cooled but are to leave the combustion chamber and travel direct into the furnace to surround the work, then water vapor content is of great importance. The lower the combustion chamber temperature, the higher is the water vapor content of the products; and vice versa, the higher the combustion chamber temperature, the lower is the water vapor content of these products of combustion.

Equilibrium Conditions and Catalysts

Practically all of the reactions between the various gases in the combustion chamber and between the gases in the furnace chamber are reversible reactions. Mention has been made of heat evolved and absorbed in the various reactions. The basic principle is that the heat evolved in a given reaction, for a given quantity of material changed by the reaction, is always equal to the heat absorbed in the reverse reaction. Equilibrium is at the point where the two opposing reactions are proceeding at the same rate. Since the two opposing reactions are proceeding at the same rate, no net change results.

Equilibrium is affected by temperature. The velocity of the reactions between the gases is increased by increasing temperatures. The increase in temperature, however, is more favorable to one reaction than to another with the result that the proportions of gases in equilibrium change as the temperature changes. In general, reactions which absorb heat are speeded up and made to go more nearly to completion by a rise in temperature and, vice versa, the reactions that liberate heat proceed farther toward completion at the lower temperatures.

The use of a catalytic agent, often referred to in connection with furnace atmosphere generators, cannot and does not change the equilibrium conditions at any temperature. The use of a catalyst

never causes a reaction to become more complete than is called for by equilibrium conditions. The catalyst simply enables the reactions to proceed more rapidly to equilibrium. Given sufficient time in the combustion chamber, the gases will arrive at equilibrium conditions according to the gas-air mix used and the temperature of the combustion chamber irrespective of the presence or the absence of a catalyst. If the volume of the combustion chamber is inadequate for the volume of gas-air mix being burned, the use of a catalyst in place of increasing the size of the combustion chamber might be desirable. The catalyst will promote the reaction toward the equilibrium point. The equilibrium point is set by the temperature and the gas-air mixture supplied.

Heat Supplied to the Combustion Chamber

Among the many possible methods of supplying heat to the combustion chamber of a gas atmosphere generator, seven are described below:

1. Preheating of the gas-air mixture or of the gas and air individually before they enter the combustion chamber. When very rich gas-air mixtures are being burned, it is not possible to add sufficient heat to the combustion chamber by this simple method of preheating the incoming gases. Some efficiency can be gained by using a heat interchanger to recover some of the heat from the gases leaving the atmosphere generator and thus decrease the added amount of heat required to maintain the proper temperatures in the combustion chamber. This procedure is applicable when the atmosphere generator gases are cooled before being introduced into the heat treating furnace.

2. By use of gas or oil-fired radiant tube heaters within the combustion chamber. Such radiant tube heaters can be made of silicon carbide refractory which is a fairly good heat conductor, or can be made of high temperature resistant metal.

3. By the use of metallic or nonmetallic electrical resistors within the combustion chamber.

4. By introducing heat from the refractory lining of the combustion chamber. If the combustion chamber is cylindrical in form, the wall can be made of metallic or nonmetallic electrical resistance material and can be maintained at a desired temperature by a current being passed through it.

5. By use of electrical resistors surrounding the combustion chamber.

6. By use of a gas or oil-fired heating chamber surrounding the combustion chamber. The air supply for this external heat would be adjusted for complete combustion. The waste heat in the gases coming from this external heating chamber could be used effectively in a heat interchanger to preheat the gas and air supplies to both the chambers.

7. By locating the atmosphere combustion chamber within the structure of a heat treating furnace in such a manner as to receive some of the furnace heat.

Whether electricity, oil or gas is used as the source of the external heat to be supplied to the combustion chamber, the temperature of the combustion chamber must be controlled. The use of automatic temperature controlling pyrometers is highly desirable. Manual control is possible. Where electricity is used as the source of the additional heat, multiple tap transformers can be used. Where gas is being used as the source of the additional heat, automatic proportioning valves are advisable.

Acknowledgments

DISCUSSION

Written Discussion: By Harry L. Daasch, professor and head of mechanical engineering, University of Vermont, Burlington, Vt.

Mr. Tour's statement on page 694 that "combustion chamber temperatures play their important role" should be expanded. Equally important are (1) the time element during which the rich air-gas mixtures are at the temperature in question and (2) the character of the surfaces with which the gases come in contact during that time and at the specified temperature. Either one of these factors may overshadow, in so far as end results are concerned, the simple and single item of temperature. Mr. Tour refers to the matter of equilibrium in a later section, but it seems this aspect should be emphasized in consideration of curves such as Fig. 1. Thus the products of combustion as shown in Fig. 1

may or may not be equilibrium values and the deviation from equilibrium is strongly influenced by the time factor and surface catalysis conditions. Equilibrium values are frequently—in fact, generally—not attained in a dynamic system as we are here discussing. The values shown in the combustion product curves should, therefore, be considered as qualitative. Precise quantitative interpretation and application to all furnace combustions at similar air-fuel ratios and temperatures may not be warranted.

The data shown may be considered from another viewpoint which will cast further doubt on its quantitative accuracy. Consider, for example, the conditions illustrated in Fig. 3. The over-all equation for the combustion reactions may be summed up:

1 Propane $+$ 8 air burn to form CO_2 $+$ CO $+$ H_2 $+$ Ill. $+$ N_2
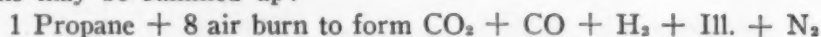
In terms of pound-mol quantities:

(360 cubic feet C_3H_8) $+$ (8 x 360 cubic feet air) burn

or

(360 cubic feet C_3H_8) $+$ (605 cubic feet (approx.) O_2)
$+$ (2275 cubic feet (approx.) N_2 burn)
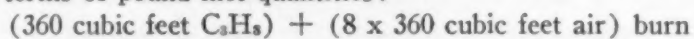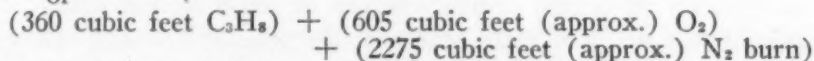
Now the nitrogen is inert and passes unchanged into the flue gases. The flue gases produced by the combustion of the 360 cubic feet of propane will contain 2275 cubic feet of nitrogen. This fact will be used subsequently.

The analyses of flue products, as shown in Fig. 3, are tabulated for several temperatures.

Table I

	1200 Degrees Fahr.	1600 Degrees Fahr.	2200 Degrees Fahr.
CO_2	4½	5	2
CO	11	15	16
H_2	6½	15	30
Ill.	4½	4	2
H_2O	13½	11	0
N_2 (By Diff.)	60	50	50
	100 Per Cent	100 Per Cent	100 Per Cent

These analyses may be converted into cubic feet. The previously developed 2275 of nitrogen produced will be used as a base.

Table II

	Cubic Feet of Gases Per 360 Cu. Ft. Propane		
	1200	1600	2200
CO_2	171	227	91
CO	418	678	728
H_2	246	678	1365
Ill.	171	180	91
H_2O	512	500	0
N_2	2275	2275	2275

These values may be converted into terms of the weight of carbon and hydrogen. Illuminants will be considered as ethylene, C_2H_4.

Table III

| | Weight of Carbon and Nitrogen Per 360 Cu.Ft. Propane | | | | | |
| | 1200 | | 1600 | | 2200 | |
	C	H_2	C	H_2	C	H_2
CO_2	5.7	0	7.6	0	3.0	0
CO	13.6	0	22.6	0	24.3	0
H_2	0	1.4	0	3.8	0	7.6
Ill.	11.4	1.9	12.0	2.0	6.0	1.0
H_2O	0	2.8	0	2.8	0	0
N_2	0	0	0	0	0	0
Totals	30.7	6.1	42.2	8.6	33.3	8.6

Now the 360 cubic feet of propane fuel contained 36 pounds of carbon and slightly more than *8 pounds of hydrogen*. While it may be said that there is no positive knowledge of the composition of the illuminants in the flue gases and that the foregoing calculations are in error to that extent, the general trends shown are not thus seriously disturbed. The calculations show almost 6 pounds and 3 pounds of carbon unaccounted for at 1200 and 2200 degrees Fahr. (650 and 1205 degrees Cent.) respectively. At the same time, over 6 pounds of carbon in excess are found for the 1600-degree Fahr. (870-degree Cent.) condition. Sooting or carbon deposition may decrease the first two unaccounted-for quantities but sooting will increase further the excess carbon calculated for the latter case.

These facts are brought forth, not to reflect on the accuracy of Mr. Tour's work, for such accuracy or inaccuracy must be expected in many gas analyses unless extreme precautions are taken. Rather, it is intended here to emphasize the danger of generally applying quantitatively such data as those shown.

The author has referred to calculations illustrating the exothermic conditions of the combustion processes discussed. The omission of sensible heat quantities has been taken as the basis of such calculation. The amount of heat that must be supplied to the combustion chamber by external means is suggested by the following illustration. The 2200 degrees Fahr. combustion of an 8:1 air-propane mixture, referred to by Mr. Tour on page 701, will be used as a basis and the volumetric data of Table II will be utilized.

Table IV

	Volumes of Flue Gas Constituents Cu.Ft.	Weight of Flue Gas Constituents Lbs.
CO_2	91	11.0
CO	728	56.6
H_2	1365	7.6
Ill.	91	7.1
N_2	2275	177.0
Total		259.3

The average specific heat of these gases may be taken as approximately 0.24 B.t.u./lb./degree Fahr. The total sensible heat at 2200 degrees Fahr. (1205 degrees Cent.) is thus:

$$H = 259.3 \times .24 \times (2200—70)\ 132,800\ \text{B.t.u.}$$

It can be shown that the production of 44 lbs. of CO_2 from C liberates 174,600 B.t.u.; the production of 28 lbs. of CO liberates 52,200 B.t.u. and the decomposition of propane to carbon and hydrogen absorbs 49,200 B.t.u. for 8 pounds of hydrogen so produced.

These values may be tabulated:

Heat of combustion

To CO_2; $\dfrac{11}{44} \times 174,600$ 43,600 B.t.u.

To CO; $\dfrac{56.6}{28} \times 52,200$ 105,500

              Total   149,100 B.t.u.

Heat of decomposition

To H_2; $\dfrac{7.6}{8.0} \times 49,200$ 46,600

Net difference available   102,500 B.t.u.

Heat to raise

     Gaseous products to 2200 degrees Fahr.   132,800

Net External Heat

     To be supplied

     Per 360 cubic feet of Fuel Burned   30,300 B.t.u.

This value neglects the heat necessary to crack a small share of the propane to illuminants. In any event, at least $\dfrac{30,300}{360}$ or over 80 B.t.u. must be externally supplied for each cubic foot of propane burned under the conditions noted.

Author's Reply

In any analysis of furnace atmospheres, the number of factors which play their part are almost infinite. To arrive at some answers as to why certain things happen in these atmospheres, it is necessary to undress the picture and reveal the basic and tangible features.

The kinetics of a reaction as affected by time and surface catalysis, as pointed out by Professor Daasch, should not be ignored. However, how are we to apply these factors of time and catalysis and materially change the situation? What order of reactions are taking place? What side reactions, counter reactions, and consecutive reactions are taking place? These are as important as temperature and catalysis.

Let us consider the factor of time and its influence on the rate of reaction as compared to temperature. Both of these are linked by the basic relation proposed by Arrhenius—

$$\frac{d \ln k}{dt} = \frac{E_2}{RT}$$

in which k is the specific reaction rate, E is a constant, R is the gas constant and T the absolute temperature. If we integrate the above, we will observe that the logarithm of the reaction rate is inversely proportional to the temperature. Thus, small increments of temperature will give large increases in rate of reaction. When we consider reactions taking place at 1600 and 2200

degrees Fahr. (870 and 1205 degrees Cent.), the time element becomes just a small percentage of the overall factor effecting the furnace atmosphere.

Let us consider surface catalysis; if anything, it will promote the speed of reaction. Though if poisons are present, it will negate its effect.

In no case is time, temperature, or catalysis able to swing a reaction beyond its equilibrium point. When such factors as elevated temperature and catalysts are present the tendency for a system to approach equilibrium is very great. Are we justified in assuming a near equilibrium condition? Temperature and surface catalysis indicate we are. Other factors may have prevented the attainment or even near attainment of equilibrium.

The data and curves that have been presented do not present an abstract picture from which to draw an abstract quantitative analysis such as Professor Daasch has done. These data were compiled under actual operating conditions in order to arrive at a better understanding of furnace atmosphere generation. Abstract assumptions are not warranted.

In the calculations presented by Professor Daasch, he more or less discredits this material because of a lack of balance between the so-called actual carbon and hydrogen in the products of combustion when compared to the amounts in the initial fuel.

His principal method of arriving at this lack of balance is by making an assumption which is not correct. Professor Daasch considers illuminants as being ethylene but in his Table III he calculates them as acetylene. Illuminants as determined by gas analysis methods may be any one of or a mixture of ethylene, propane, propylene, butane, butylene, acetylene and liquid hydrocarbons (mostly benzene). By assuming the illuminants to be any one or a mixture of these, one can end up with a carbon-hydrogen balance which shows a loss, the same amount as started with, or an amount in excess of that which was started with.

The following table shows what happens to the totals of Professor Daasch's Table III at 1200 degrees Fahr. when different illuminant assumptions are made.

Illuminant Assumption	Total in Products	
	Carbon	Hydrogen
Methane, CH_4	25.0	8
Ethylene, C_2H_4	30.7	8
Acetylene, C_2H_2	30.7	6.1
Propane, C_3H_8	36.4	11.8
Propylene, C_3H_6	36.4	9.9
Benzene, C_6H_6	53.5	9.9

The above indicates that one can juggle out an answer to suit one's self. It is not meant or implied or stated that Professor Daasch has juggled figures. It is merely pointed out that assumptions are dangerous things and can give very misleading answers.

A proper illuminant assumption would require inclusion of a number of these hydrocarbons and at different temperatures they would be present in different ratios.

Another item which Professor Daasch has completely disregarded is the fact that air contains moisture. Thus, the hydrogen present in the products should be more than based on the hydrogen content of the propane.

There is little to say about Professor Daasch's thermal calculations. The paper distinguishes between the heat of reaction and sensible heat. The discussion of exothermic versus endothermic reactions is based on the reactants being at the same temperature level as the products. It is recognized that heat must be supplied to the reactants to bring them up to the temperature at which the reaction is to take place. The heat given off or absorbed as a result of a chemical change is distinct and different from sensible heat. Sensible heat is no measure of exothermicity or endothermicity of a reaction.

What Professor Daasch has shown is that the sensible heat absorbed by totally inert nitrogen is considerable. At 2200 degrees Fahr. (1205 degrees Cent.) for his specific example and using his stated figure of 0.24 for specific heat the inert nitrogen has required

$$177 \times .24 \times 2130 = 90{,}472 \text{ B.t.u.}$$

Professor Daasch finds only 60,170 B.t.u. available from the reaction and must supply 30,300 B.t.u. from some other source. The reactions *per se* are strongly exothermic by Professor Daasch's own calculations. The inert nitrogen requires external heat.

WATER VAPOR IN FURNACE ATMOSPHERES

By Sam Tour

Abstract

Water vapor is one of the major products resulting from the combustion of fuel gas and air mixtures. The standard methods of gas analyses applied to furnace atmospheres give compositions of the gases as-cooled to room temperature. During this cooling of the gases, the surplus water vapor is condensed to water and removed until the remaining gases are saturated at the temperature of analysis. Assuming that no other gas reactions take place during cooling, the results could be recalculated to correct for this loss of water if the total original amount of water were known. With certain simple fuel gases and known air-gas ratios, the total water vapor can be calculated. Results show that in some cases the actual water vapor content in the products of combustion of rich gas and air mixtures as used for heat treating furnace atmospheres may contain as much as 18 per cent of water vapor. The overall gas atmosphere composition is affected by the water vapor present. By cooling to remove the water and then reheating, the composition may be caused to change. By removing water vapor and reheating, it is possible to reduce the amounts of residual hydrogen and carbon dioxide and increase the residual carbon monoxide. The carburizing or decarburizing tendencies of the furnace atmosphere gases can be influenced and controlled to a great extent by the dehydrating reheating and recirculating through the furnace of the gaseous products of combustion of rich mixtures of fuel gas and air.

A DISCUSSION of the problem of the heat treatment of iron and steel in a neutral atmosphere was given by A. H. White and H. T. Hood in 1915 (1)[1]. These authors pointed out that the products of combustion of gas and air-contained water vapor as well as carbon dioxide and that both are oxidizing agents. They suggested that a neutral atmosphere would be one in which the total of the re-

[1] The figures appearing in parentheses pertain to the references appended to this paper.

ducing gases, carbon monoxide, hydrogen and methane, would be greater than the total of the oxidizing gases, carbon dioxide and water. They gave the results of numerous calculations and experiments with an unenriched coal gas with an average heating value of somewhat over 600 B.t.u. burned with air in the ratio of 1 cubic foot of gas to 2 cubic feet of air. Burning this mixture in an apparatus in which the combustion took place at a temperature of approximately 2100 degrees Fahr. (1150 degrees Cent.), they report a resulting composition of gases approximately as follows:

	Per Cent
Nitrogen (N_2)	52.0
Carbon Dioxide (CO_2)	2.5
Carbon Monoxide (CO)	12.0
Hydrogen (H_2)	16.0
Methane (CH_4)	2.0
Illuminants	0.5
Water Vapor (H_2O)	15.0

Treating high carbon steel wire in this atmosphere, they found that oxidation of the metal did not occur but that severe decarburization did result. They concluded—"a neutral atmosphere is produced when approximately one volume of illuminating gas is combined with two volumes of air; a mixture so rich that it will not burn unless preheated. This atmosphere, although neutral to iron, decarburizes steel slowly at forging temperatures; but it is a much less active decarburizing agent at this temperature than the ordinary furnace atmosphere, and may be rendered still less active by using a mixture richer in gas."

Throughout the years since 1915, the literature abounds with references to the effect of water vapor in furnace atmospheres used for the heating of steel. An interesting summary of the situation was given in the Journal of the Society of Chemical Industry Transactions, Feb. 25, 1927 (2). Part II of the above article points out the importance of the reaction between hydrogen and carbon dioxide to form additional water vapor.

A further interesting and informative review of the general situation was given by Stansel and Dantsizen (3) in the "General Electric Review," issues of March 1929 and May 1929. Most of the information contained in these original reviews by Stansel and Dantsizen are given in the book by Stansel (4). By grouping a number of equilibrium ratio curves on one chart, Stansel has shown that the ratios between various components of a furnace atmos-

phere which will not scale steel are radically different from the ratios required if the steel is not to be carburized or decarburized. In other words, the prevention of scaling can be accomplished with an entirely different set of ratios of components of the atmosphere than may be required for the prevention of carburizing or decarburizing.

In the heat treatment of tool steels, the problem of carburizing versus decarburizing is all important. It is fair to say that the modern practice of heat treating tools in controlled atmosphere furnaces is a development of the past 12 years since the introduction of the Hayes Certain Curtain furnace in 1928. The heat treatment of delicate tools of high speed steel in furnaces of this type was later described by the writer in 1930 (5). The presence of water vapor in furnace atmospheres and the effect of water vapor on tool steels being treated was again pointed out at that time. The importance of water vapor in heat treating furnace atmospheres was stressed by this author in a paper published in 1932 (6). While it is possible to determine hydrogen, methane and water vapor in furnace atmospheres, the fact remains that a majority of so-called furnace atmosphere analyses consist only of determinations made with the ordinary Orsat apparatus which is limited to oxygen, carbon dioxide and carbon monoxide. The literature contains some information regarding hydrogen, methane and illuminants present in various furnace atmospheres. The literature is almost wholly lacking in data regarding water vapor content of the atmospheres.

CALCULATIONS OF WATER VAPOR CONTENT

In order to be able to calculate the quantity of water vapor which is formed and, therefore, included in the products of combustion, it is necessary to know the relationship between the volume of gases entering the reaction and the volume of gases resulting from the reaction of combustion.

White and Hood (1) in their article in 1915 showed quite clearly the difficulty in attempting to calculate the volume of products of combustion resulting from the burning of a complicated manufactured gas with limited volumes of air. When the gas being burned is a single component gas, such as methane (CH_4), or propane (C_3H_8), the problem is not so difficult. When rich gas-air mixtures are used, however, it is still impossible to calculate on the

basis of ratio of actual volume of products of combustion compared to volume of gases being burned. This disturbance of volume relationship is due to the fact that the methane or propane does not burn completely to the ordinary products of combustion but is partly transformed into carbon, soot and complex hydrocarbons classed under the general terminology of "illuminants." A conservative method of calculating the amount of water vapor present in the products of combustion is based upon the hydrogen content of the products of combustion and the known relationship between hydrogen and carbon in the gas being burned. By this method, the calculated amount of water vapor must be lower than the true amount present in products of combustion. It is lower than the true amount because all the carbon in the gas being burned does not show up as carbon monoxide and carbon dioxide in the products of combustion.

In the case of methane, each volume of methane (CH_4) which is burned must yield two volumes of hydrogen plus water and one volume of carbon monoxide plus carbon dioxide. In the products of combustion the total volume of hydrogen plus water vapor present must equal at least double the volume of carbon dioxide plus carbon monoxide present. To the extent that some carbon has been lost in the form of soot or held in the form of illuminants of higher carbon content than methane, this calculation of water vapor present will yield a low figure. The minimum water vapor figures must be those which when added to the hydrogen volume present will equal a volume double that of the carbon monoxide plus carbon dioxide present. It might be well to point out that the amount of carbon which is lost as soot, pitch, coke, higher hydrocarbons, etc., is closely associated with the temperature of the combustion chamber.

The effect on the gas composition of varying the ratio of air for combustion with natural gas is shown in the form of a chart in a paper by B. W. Gonser (7). He refers to these curves as "Heyn." Assuming that the natural gas is practically all methane, we can start with the "Heyn" curves and calculate the water vapor which must have been present. In view of the fact that water vapor is removed in the ordinary process of making gas analyses, the actual percentages found for the various constituents of the gas being analyzed are based upon the residual volume after the water vapor has been removed. Having calculated the water vapor volume which must have been present in the "Heyn" experiments, we can recalculate the true percentages of each of the constituents which

he actually analyzed for and plot a revised set of curves for the various components present. It is thus possible to show the true effect on the gas composition of varying the ratio of air for the com-
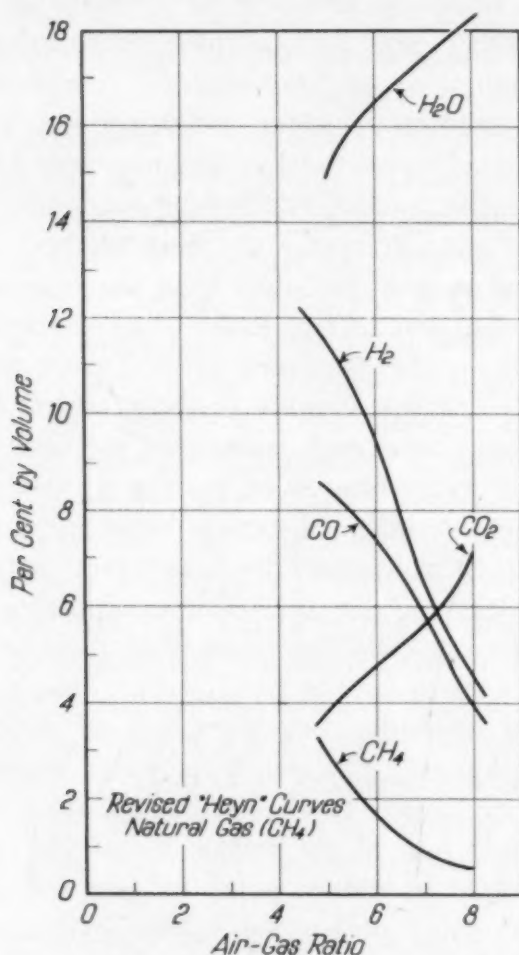
Fig. 1—Revised "Heyn" Curves. Natural Gas (CH_4).

bustion of natural gas. This is shown in Fig. 1 under the caption "Revised Heyn Curves." It will be noted that the water vapor present is several times the volume of carbon dioxide present. It is unfortunate that we have no information with regard to the combustion chamber temperatures in connection with the original "Heyn" curves.

Burning propane gas (C_3H_8) with various ratios of air to gas in a gas curtained furnace and with the combustion chamber maintained at approximately 1600 degrees Fahr. (870 degrees Cent.), the usual gas analyses for carbon monoxide, carbon dioxide, hydrogen and illuminants were made. The results are shown in Fig. 2.

From these results the amount of water vapor was calculated. These
calculations for water vapor were based upon the fact that for each
three volumes of carbon monoxide plus carbon dioxide present,
there must result at least four volumes of hydrogen plus water
vapor. Having calculated the water vapor present in this fashion
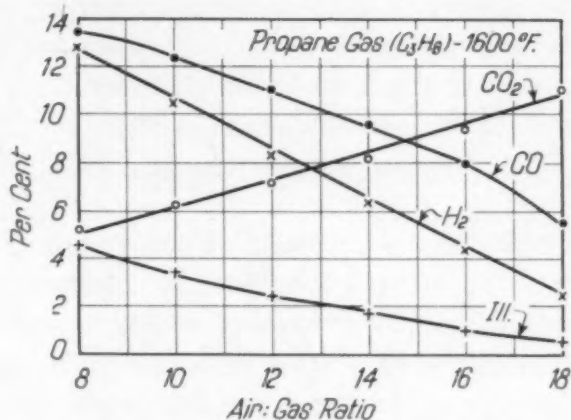
Fig. 2—Effect of Changes in Air-Gas Rates.
Propane Gas (C_3H_8) 1600 Degrees Fahr. (870
Degrees Cent.).
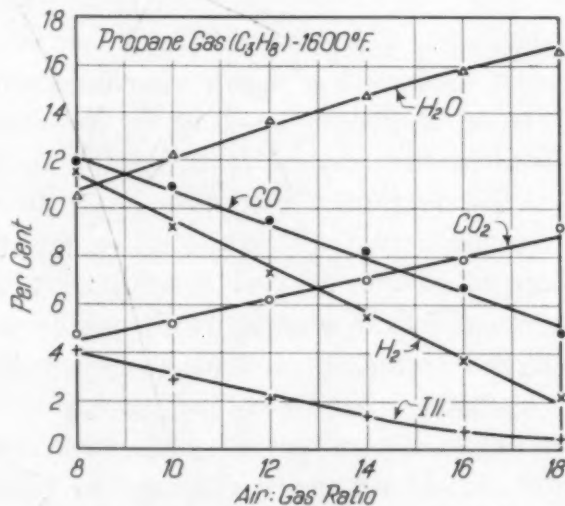
Fig. 3—Effect of Changes in Air-Gas Rates.
Propane Gas (C_3H_8) 1600 Degrees Fahr. (870
Degrees Cent.). Corrected for H_2O.

and then having used this factor to correct the analyses for the other
gases present, the revised curve for the burning of propane at 1600
degrees Fahr. (870 degrees Cent.) with different air to gas ratios
from 8 parts to 18 parts of air to 1 of gas are shown in Fig. 3. It is
evident that water vapor is one of the principal gases present.

As the amount of water vapor contained in the gas and air

mixtures supplied for combustion amount to less than 3 per cent and as the combustion reaction itself develops several times this quantity of water, it is quite obvious that the use of dried air and gas for combustion will be of no material help to reduce the water vapor content of the products of combustion. That this situation is not fully realized in industry is evident by the number of installations where column or tower driers of various types are being used to dry the air on its way to the combustion chamber.

EQUILIBRIUM RATIOS

Previous mention has been made of the grouping of a number of equilibrium ratio curves on one chart by Stansel. His selection of curves has been copied by a number of other authors. For the oxidation reduction curve for ratios of water to hydrogen, Stansel selected to use curves represented by the work of Murphy and Jominy and to disregard the curves by Eastman and Evans. Murphy and Jominy found much less water permissible if oxidation or scaling was to be avoided. In connection with the curves for the carburizing and decarburizing reaction resulting from various ratios of methane to hydrogen, Stansel has selected a curve which represents activity toward carbon and assumes that is the same as activity toward a steel saturated with carbon at the temperature in question. The equilibrium ratios have been determined for three unsaturated steels by Sykes. In connection with the equilibrium between carbon dioxide and carbon monoxide, Stansel again selects a curve representing activity toward carbon and rightfully points out that values for unsaturated or low carbon steels have not been determined. A similar grouping of curves but extending to higher temperatures, with the addition of the Sykes curves for unsaturated steels and with the addition of certain notations, is shown in Fig. 4.

For the atmosphere to be neither carburizing nor decarburizing toward steel in the furnace requires a delicate balance between the methane and hydrogen present. For example, with a 0.95 per cent carbon steel at 1475 degrees Fahr. (800 degrees Cent.), 1 per cent of methane is required to neutralize the decarburizing activity of 20 per cent of hydrogen in the atmosphere. With a 20 per cent hydrogen content, more than 1 per cent of methane will give a carburizing action while less than 1 per cent methane will give a decarburizing action. At 1475 degrees Fahr. (800 degrees Cent.) for

perfect neutrality to 0.95 per cent carbon steel, Sykes shows a required ratio of 20 to 1 between hydrogen and methane. At 1650 degrees Fahr. (900 degrees Cent.) 1 per cent of methane will neutralize the decarburizing activity of 50 per cent of hydrogen.

The Rhead Wheeler Stansfield curve for CO_2-CO-C shows that
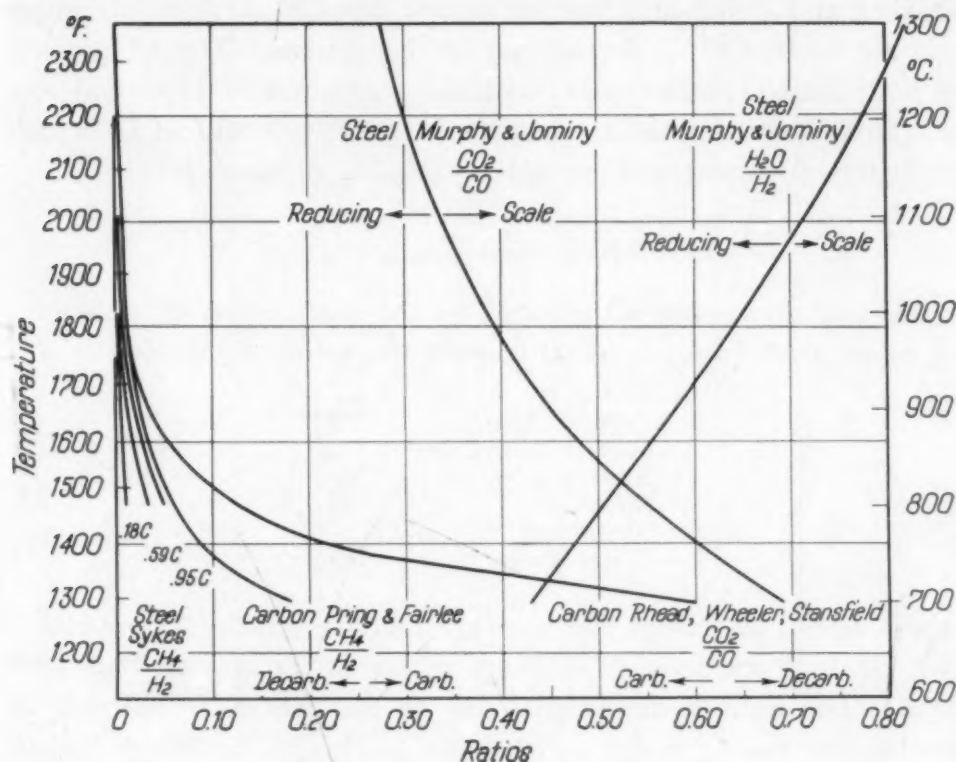
Fig. 4—Decarburizing and Scaling Ratio Curves.

at 1475 degrees Fahr. (800 degrees Cent.) for each 1 per cent of CO_2 present, there must be at least 8 per cent of CO or decarburization will result. At 1650 degrees Fahr. (900 degrees Cent.) each 1 per cent of CO_2 requires almost 30 per cent of CO.

The Murphy and Jominy curve for CO_2-CO-Fe shows at 1475 degrees Fahr. (800 degrees Cent.) scaling due to CO_2 will result unless CO is present in at least twice the amount of the CO_2. At 2000 degrees Fahr. (1095 degrees Cent.), however, the CO present must be three times the CO_2 if scaling is to be avoided.

The Murphy and Jominy curve for H_2O-H_2-Fe shows that at 1475 degrees Fahr. (800 degrees Cent.) scaling due to H_2O will result unless H_2 is present in at least twice the amount of H_2O. At 2000 degrees Fahr. (1095 degrees Cent.), the H_2 required to prevent scaling due to H_2O is 1.8 times the amount of H_2O.

Unfortunately these curves are based upon the presence of only two reacting gases at one time. If more than two reacting gases are present and one of them enters into reactions with more than one of the others present, we have a difficult situation.

CO_2 reacts with both H_2 and CH_4. It is readily apparent that the Sykes and Pring and Fairlee curves for CH_4-H_2 are no longer applicable when CO_2 is introduced in the system. The CO_2 reacts with both the CH_4 and the H_2 with the formation of H_2O and CO. The equilibrium conditions applicable to CO_2-CO and H_2O-H_2 are immediately superimposed upon the CH_4-H_2 system.

Reactive Gases

Furnace atmospheres produced by the combustion of rich mixtures of air with fuel gas or oil contain the following gases:

1.—Nitrogen	N_2
2.—Carbon Dioxide	CO_2
3.—Carbon Monoxide	CO
4.—Hydrogen	H_2
5.—Methane	CH_4
6.—Illuminants	?
7.—Water Vapor	H_2O

Of these seven, all except nitrogen are reactive gases. "Illuminants" consist of hydrocarbons of various ratios of carbon to hydrogen content. The light hydrocarbons can be considered as reacting in somewhat the same manner as methane (CH_4). The heavy hydrocarbons can be considered as reacting in a manner similar to carbon.

The six reactive gases enter into six reactions which must be considered as follows:

$$1.—CO_2 + H_2 = CO + H_2O$$
$$2.—CO_2 + CH_4 = 2CO + 2H_2$$
$$3.—CO_2 + C = 2CO$$
$$4.—H_2O + CH_4 = CO + 3H_2$$
$$5.—H_2O + C = CO + H_2$$
$$6.— \quad CH_4 - C + 2H_2$$
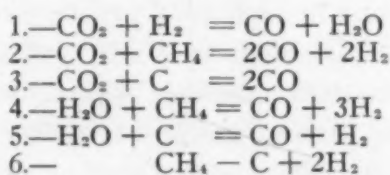
Dehydration and Reheating

Figs. 1 and 3 show the large amounts of water vapor present in the products of combustion of various mixtures of air and methane and air and propane. If the gases are cooled, as in the carrying out of the ordinary gas analyses, the excess water vapor present condenses and is removed. The amount of water vapor remaining in the gases after cooling is a function of the temperature to which

the gases are cooled. The remaining water vapor content of the gases
is indicated in Fig. 5 which is the vapor pressure curve of water
vapor plotted in terms of per cent water vapor at various temper-
atures at sea level. It will be noted that if the gases are cooled to
50 degrees Fahr., they will retain 1.2 per cent of water as water
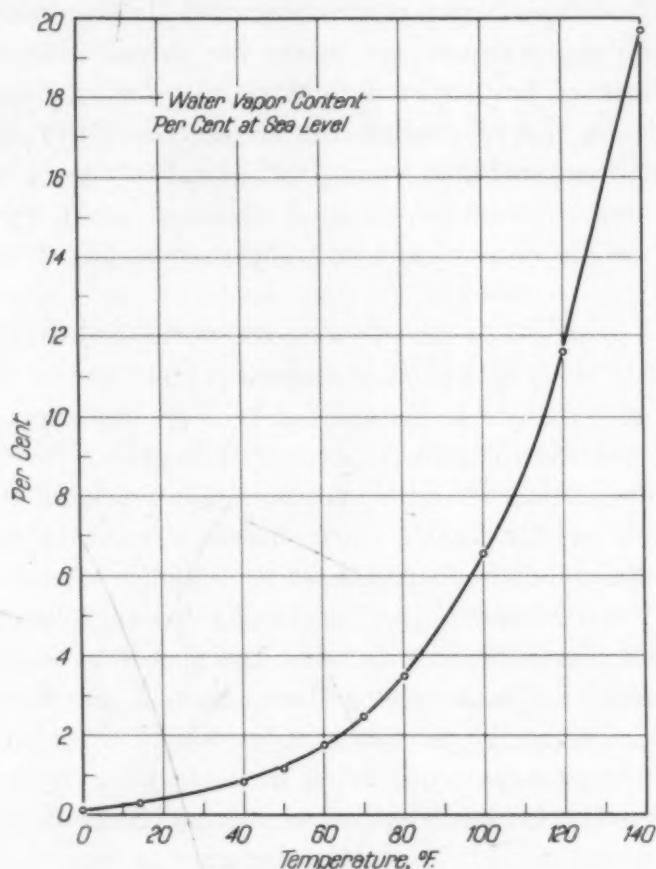
Fig. 5—Water Vapor Content Per Cent at Sea Level.

vapor. If they are cooled to only 70 degrees Fahr., they will retain
2.5 per cent of water vapor. If cooled to only 100 degrees Fahr.,
they will retain 6.5 per cent of water vapor. Referring to Figs. 1
and 3, it will be noted that all of the gas mixtures contain well over
10 per cent of water. If the gases are removed from the combustion
chamber and cooled to room temperature, say 70 degrees Fahr., they
will lose all but 2.5 per cent of their moisture. If these cooled and
somewhat dehydrated gases are now reintroduced into a furnace
operating at heat treating temperatures, they will be in an unstable
condition and will begin to react with each other in order to re-
establish equilibrium between the various reactive gases.

As the ordinary products of combustion of rich mixtures of gas and air contain both hydrogen and carbon dioxide and as these two gases will react to produce water vapor when the dehydrated gases are reheated to furnace temperatures, it is evident that perfectly dry atmospheres in the furnace are impossible. That this is not fully realized in industry is demonstrated by the number of installations using column or tower driers for dehydrating such products of combustion before introduction into furnaces as furnace atmospheres. As simple cooling to 50 degrees Fahr. will reduce the moisture content to 1.2 per cent, and as reheating the mix in the furnace may create 3 to 5 per cent of water, it would seem evident that the expense of dehydration to a dew point below zero is unwarranted.

This basic principle of dehydrating the gases and reheating them so that they may react and then introducing them as the furnace atmosphere around the work being heat treated has been developed by one of the electric furnace builders and is called "recirculation." The actual construction is quite simple. The products of combustion of the rich gas-air mixture are drawn out of the combustion chamber through a cooler where the water vapor is condensed. The dehydrated gas is then pumped into a small reheating chamber within the furnace. In this reheating chamber the gases are brought up to furnace temperature, react among themselves to re-establish equilibrium and then enter the furnace proper where they form the atmosphere surrounding the work being heat treated. By putting the combustion chamber beneath a curtain slot at the entrance to the furnace and, therefore, inside of the furnace proper it is possible to operate the circulating pump at such a speed as to handle a larger volume of gases per hour than is being introduced through the burners. By doing this, a considerable amount of recirculation is obtainable and a considerable quantity of the furnace gases may be used over and over again with the addition of some fresh products of combustion for each pass through the furnace.

The ordinary Orsat analyses on the furnace gases being recirculated and dehydrated in this fashion show a decided decrease in CO_2 content and an increase in CO content. The general situation with regard to this change in CO_2 content and with regard to the further question of soot or carbon deposition will be better understood if we consider the various reactions involved. The six reactions to be considered have already been listed.

Reaction 1: The gases leaving the combustion chamber contain a considerable percentage of water and, therefore, are stable with a considerable percentage of CO_2. Removal of this water in the circulating system destroys the equilibrium and upon reheating of the gases, the reaction proceeds towards the elimination of some of the carbon dioxide and the formation of more water. The CO_2 content of the gases leaving the dryer will, therefore, be higher than the CO_2 content of the gases in the furnace chamber after they have been reheated. Each volume of carbon dioxide which is removed by this reheating produces a like volume of water. It will be noted that this reaction is speeded up by the removal of water and by the increase in hydrogen resulting from the use of richer gas-air mixtures. It will also be noted that an increase in carbon monoxide will tend to retard this reaction.

Reaction 2: CO_2 combines with methane to produce carbon monoxide and hydrogen. An increase in methane will result in a speeding up of the elimination of CO_2 on reheating. This reaction produces hydrogen which will speed up Reaction 1 for the further elimination of carbon dioxide.

Reaction 3: This is a reaction between carbon dioxide and solid carbon and is controlled largely by temperature. Any increase in temperature will speed up this reaction and will tend to eliminate carbon dioxide and to form carbon monoxide. As carbon monoxide is increased, there will be a tendency to decrease the speed of this reaction and more CO_2 will be stable in the presence of carbon. This effect of excess carbon monoxide, however, is small as compared to the effect of temperature. A slight increase in temperature will cause the reaction to proceed even in the presence of considerable amounts of carbon monoxide.

Reaction 4: This is a reaction between the moisture and methane. Increase in moisture content resulting from Reaction 1 automatically speeds up Reaction 4. Reaction 4 forms hydrogen which automatically speeds up Reaction 1. It is obvious that temperatures are important in all of these reactions and that the higher the temperature the faster the reaction takes place and the further it goes to the right.

Reaction 5: From this reaction, it is evident that carbon present will automatically take care of some of the moisture resulting from Reaction 1 and will, therefore, by creating Reaction 5 speed up Reaction 1. It is again evident that Reaction 5 produces hydrogen

which also speeds up Reaction 1. The carbon for Reactions 3 and 5 can come only from Reaction 6.

Reaction 6: This is the straight cracking of methane. Similar cracking reactions might be shown for the other hydrocarbons besides methane but all can be expected to act alike. Methane is the one reaction which produces carbon and, therefore, soot in the furnace. To the extent that methane cracks to provide carbon to supply Reaction 3 and Reaction 5 and thus tend to eliminate both carbon dioxide and moisture, we have a desirable reaction in 6. To the extent that Reaction 6 produces more carbon than can be taken care of by the Reaction 3 and 5, we have a sooty condition in the furnace.

The speed with which Reaction 6 takes place is a function of temperature. The amount of methane which will be stable in the presence of hydrogen is a function of the temperature. The higher the temperature, the lower the amount of methane which will be stable for the same amount of hydrogen. It will be seen that this reaction produces hydrogen. To the extent that this hydrogen is consumed by Reaction 1 in the removal of carbon dioxide, we will tend to crack down more methane and produce more carbon or soot. The amount of methane in the products of combustion is considerably controlled by the temperature of the combustion chamber. The higher the temperature of the combustion chamber, the lower the amount of uncracked methane which will come out of the combustion chamber, and the less will be the trouble due to soot and carbon deposits in the furnace.

The principal difficulty in the study of atmospheres is that these six reactions all take place and each affects the other one. It is not proper to consider the individual reactions as being independent of the other five and attempt to predict what the equilibrium ratios may be between methane and hydrogen, for example, without regard to the amount of CO_2 present, or between CO_2 and hydrogen without regard to the amount of methane present. Attempts to use many of the curves in the literature, such as Stansel, have been misleading because these oxidization and reduction curves are based upon experiment runs with synthetic mixtures having only two constituents present, instead of having all of the constituents with which we have to deal.

Tests have shown that with dehydration and recirculation as described, the amount of CO_2 in the furnace chamber can be reduced to 1 per cent or less. On the assumption that the principal reaction

which accomplishes this reduction in CO_2 is Reaction 1, the reaction between carbon dioxide and hydrogen with the formation of water, we can calculate what happens with the various air-gas ratios as shown in Fig. 1. The result is shown in Fig. 6. Obviously when practically all of the hydrogen is consumed, there can be no further reduction of carbon dioxide by Reaction 1. This is shown by the
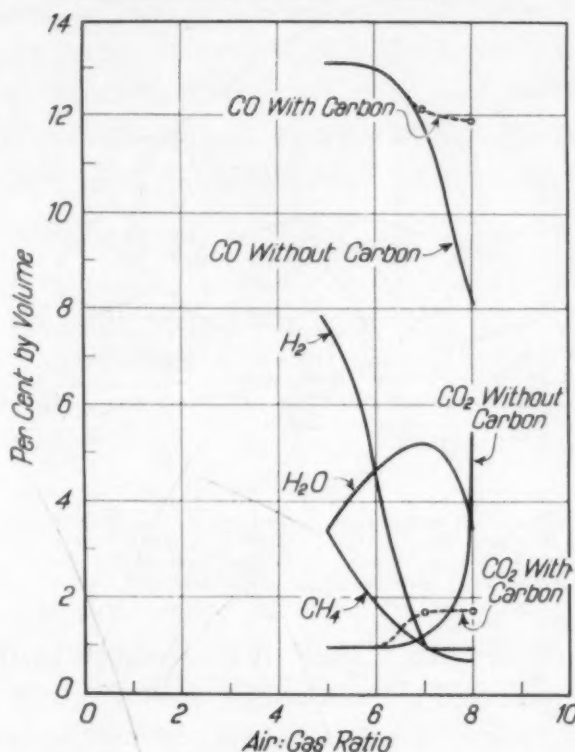

Fig. 6—Effect of Dehydration and Recirculation on Natural Gas (CH_4) Burned with Air.

solid lines in Fig. 6. However, if carbon has been deposited in the reheating chamber, the carbon can supply the material for Reaction 3 to proceed and the CO_2 content can be further reduced. The extent to which this reaction takes place is a function of temperature and the equilibrium condition between CO_2, CO and carbon. This is covered by the Rhead, Wheeler and Stansfield curve in Fig. 4. At 1475 degrees Fahr. (800 degrees Cent.), the CO_2 content will be one-eighth of the CO content. In Fig. 6, the solid line shows the CO_2 and CO calculated on the basis of the reaction of CO_2 with hydrogen alone. The dotted line shows the location in the presence of excess carbon. The dotted line is actually the line encountered in actual practice due to the ever-present free carbon in the burning of rich mixtures of gas and air.

This same treatment applied to the combustion products of the propane gas air mixtures shown in Fig. 3 results in the rearrangement of gases as shown in Fig. 7.

The net result of this dehydration and recirculation is quite evident. The amounts of oxidizing gases, carbon dioxide and water
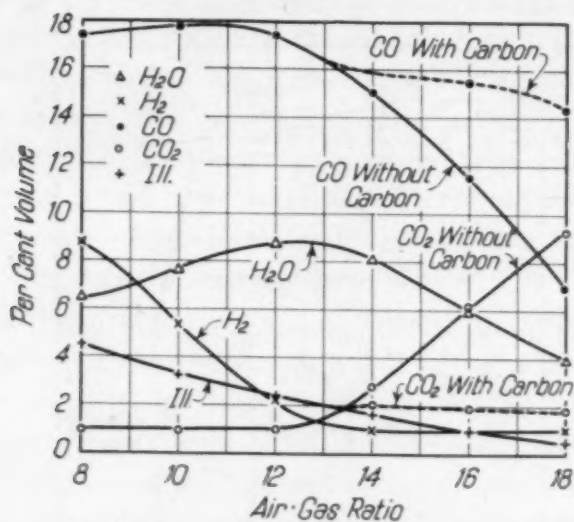
Fig. 7—Combusting, Dehydrating and Reheating Propane Gas (C_3H_8). Gases of Curves in Fig. 3 at 70 Degrees Fahr. (2.5 Per Cent H_2O) Reheated to 1475 Degrees Fahr. (800 Degrees Cent.).

vapor, have been reduced, the amount of the decarburizing gas, hydrogen, has been reduced, and the amount of desirable carbon monoxide gas, CO, has been increased. In this manner it is possible to obtain an atmosphere which is nonscaling towards any steel. By controlling gas-air ratios, combustion chamber and reheating chamber temperatures, a controlled combination of CO and methane can be obtained as needed, for each type of tool steel to be heat treated. As one example, it is possible to obtain an atmosphere sufficiently rich to be nonscaling and nondecarburizing to the high carbon high chromium steels. Clear atmospheres can be obtained in the furnace with carbon dioxide content well below 1 or 2 per cent and with carbon monoxide content of 20 per cent or more.

It has been proposed that furnace atmospheres be generated by burning gas-air mixtures only slightly richer than required for perfect combustion, removing excess water by cooling, removing the carbon dioxide by absorption in a separate absorption tower and then complete removing of residual water in additional towers. This will produce a high nitrogen atmosphere substantially free of hydrogen

and carbon monoxide. If the carbon dioxide removal and the dehydration are not both 100 per cent perfect, the product will have an oxidizing or scaling reaction on steel. If a richer gas-air mixture is used than that required for perfect combustion, a sufficient amount of hydrogen and carbon monoxide can be obtained in the products of combustion so that simple cooling and reheating will accomplish substantial removal of the carbon dioxide and the expensive carbon dioxide absorption tower system is not necessary. In view of the fact that some excess hydrogen can be allowed to remain to neutralize any scaling activity of a small percentage of moisture, it also becomes unnecessary to go the expense of column or tower dehydration.

Multiple Recirculation

By operating the recirculating pump at a rate to handle several times the volume of gases which are being burned per hour and introduced into the system, it is possible to recirculate the bulk of the gases a number of times. By doing this, other advantages are obtained.

To obtain the rich atmospheres desired for tool steels, the gas-air mixture which must be burned is so rich that it will not support combustion by its own heat liberation. This does not mean that the mixture being burned is such that the reactions are endothermic (absorb heat). Actually the reactions are all exothermic. The amount of heat liberated, however, by these reactions is insufficient to raise the incoming gas-air mixture to the desired furnace temperature or to an adequate combustion temperature. By locating the combustion chamber below the neck of the heat treating furnace and recirculating a large volume of the furnace atmosphere, it is possible to mix a large volume of hot furnace gases with the incoming gas-air mixture and thus supply heat and raise the temperature of the incoming mix so that better combustion will take place. If the volume of gases being circulated is just equal to the volume developed by the combustion of the fresh gas and air being sent into the combustion chamber, less the water removed by dehydration, we have circulation only, not recirculation. By operating the pump so as to draw a larger volume than is being introduced in the form of fresh gas and air into the combustion chamber, we have recirculation. This supplies heat to the fresh mixture to aid in its combustion. Additional water formed by the gas reactions during reheating is removed

in the recirculating system. For example, if the volume of gases being handled by the recirculating system is three times the volume of the fresh gases being introduced, the combustion chamber receives hot gases equal to double the volume of the incoming cold gases to be burned. This is a decided help in the burning of this cold mix. At the same time, the water vapor content of the gases from the combustion chamber plus the added water vapor due to the reheating and carbon dioxide removal are removed before the gases are reheated and reintroduced into the furnace.

ACKNOWLEDGMENTS

References

1. A. H. White and H. T. Hood, American Gas Journal, Nov. 15, 1915.
2. "The Influence of Atmosphere and Temperatures Upon the Scaling of Steel, Part I—Scaling by Air, Water Vapor, and Carbon Dioxide; Part II—Prevention of Scaling by Hydrogen and Carbon Monoxide," Journal, Society of Chemical Industry Transactions, Feb. 25, 1927.
3. N. R. Stansel and C. Dantsizen, General Electric Review, March and May, 1929.
4. N. R. Stansel, "Industrial Electric Heating," John Wiley & Sons, Inc., 1933.
5. S. Tour, Fuels and Furnaces, September 1930.
6. S. Tour, "Heat Treating Furnace Atmospheres," Metals and Alloys, December, 1932.
7. B. W. Gonser, "The Status of Prepared Atmospheres in the Heat Treatment of Steel," Heat Treating and Forging, May 1939.

DISCUSSION

Written Discussion: By Harry L. Daasch, professor and head of mechanical engineering, University of Vermont, Burlington, Vt.

Mr. Tour has been able to present a great deal of information on the fundamentals of combustion in a very compact form.

While physical chemists have evolved equilibrium data for individual systems such as CO_2CO-C or CH_4-H_2-C, apparently none have been anxious to become involved in the complexities of a single system involving the seven gases noted by Mr. Tour.

The writer would, therefore, warn against conclusions too quickly drawn by abstract consideration of these individual combustion reactions noted. Mr.

Tour's statements on page 722 are in agreement with this thought and he recognizes the danger of making "the assumption that the principal reaction . . . is Reaction 1." The following notes may suggest this assumption to be in error.

For example, consider Reactions 3 and 5:

$$CO_2 + C \rightarrow 2CO \qquad\qquad 3$$
$$H_2O + C \rightarrow CO + H_2 \qquad\qquad 5$$

It is well known that, at the temperature range here discussed, the reduction of carbon by CO_2 is over twice as fast as the reduction of the same carbon by water vapor. The former is therefore the most important and effective reaction.

Again consider Reaction 1

$$CO_2 + H_2 \leftrightarrows CO + H_2O$$

It is known that the equilibrium values for this reaction at 1600 degrees Fahr. (870 degrees Cent.) are approximately as shown in Table A.

Table A

CO_2	2 Per Cent
H_2	50 Per Cent
CO	47 Per Cent
H_2O	1 Per Cent

An approximate equality in CO and H_2 is shown at 1600 degrees Fahr. (870 degrees Cent.) by Fig. 3. However, the proportions of CO_2 and of H_2O (as of Fig. 3) are about ⅓ of the CO or the H_2. In other words, the CO_2 and H_2O are much greater than the equilibrium proportions given in Table A.

As a matter of fact, the drying of such flue gas mixtures as quoted in Fig. 3 will simply bring the proportions of moisture nearer to 1600 degrees Fahr. (870 degrees Cent.) equilibrium value, in so far as Reaction 1 is concerned.

Now, Reaction 1 is quite slow at the 1600 degrees Fahr. (870 degrees Cent.) temperature range. That other reactions overshadow it in speed is shown by the already quoted figure on equilibrium. Furthermore, as already stated, the reduction of CO_2 by C, especially finely divided soot, is very rapid. The excess CO_2 referred to above is thus by its mass action likely to further speed Reaction 3 toward the right. Finally, the increased CO so produced may well react, though slowly, with the remaining H_2O, as per Reaction 1, action to the left.

The writer would prefer to consider Mr. Tour's Reactions 6 and 1 as sufficient without Reaction 2. The sum of the first two will, of course, equal the latter. Likewise, Reaction 4 should not be shown. In other words, methane decomposes:

$$CH_4 \rightarrow C + 2H_2$$

and these products may react with CO_2

$$CO_2 + H_2 \rightarrow CO + H_2O$$
$$CO_2 + C \rightarrow 2CO$$
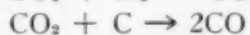
So far as the writer can determine, a reaction such as given by Mr. Tour's Reaction 4 will occur at a speed, effective for consideration in terms of furnace atmospheres and at a temperature of 1600 degrees Fahr. (870 degrees Cent.), only with the aid of a catalyst such as pure nickel.

All this is, just as is the author's discussion, useful only to secure a general

conception of the processes. Such reasoning is really dangerous if proportions of end products of all these reactions are being forecast.

The present writer would, therefore, agree with the end results presented by Mr. Tour in so far as they concern the influence of carbon. In the light of what has been said here, there might be disagreement as to the mechanism of accomplishment. It might better be assumed that Reaction 3, rather than Reaction 1, is primary in the reduction of CO_2 in recirculated furnace gases.

Finally, one might question the broad statement on page 725 that all of "the reactions are exothermic." While the initial combustion of CO or H_2 with air may be so, many of the secondary reactions alluded to and here discussed, as well as initial decomposition of hydrocarbons which may precede combustion, are endothermic. This fact must be recognized in burner and furnace design and operation.

Written Discussion: By Bruce W. Gonser, metallurgist, Battelle Memorial Institute, Columbus, Ohio.

Some explanation may be needed regarding the "Heyn" curves to which Mr. Tour refers. These were given by H. M. Heyn[1] of the Surface Combustion Company. The curves showed the gas compositions resulting from the combustion of natural gas with a varying gas-air ratio as they are obtained from a commercial furnace atmosphere generator. Water vapor was given as a constant since all but about one per cent was removed by cooling the gas in the condenser of the generator, regardless of the air-gas ratio. This is obvious from the original chart. In Mr. Tour's Fig. 1, this same set of curves is given after compensation has been made for the total water vapor formed in partial combustion. This gives the gas that would be formed in the combustion chamber of an atmosphere generator or by direct firing into a furnace at the same temperature.

Oral Discussion

W. E. KINGSTON :[2] I would like to ask Mr. Tour his opinion on this reaction, whether he could predict the reaction between a stable compound of carbon and silica, such as used in silicon carbide resistors, and a highly reducing atmosphere such as dissociated ammonia saturated with water vapor at a temperature of 100 degrees Fahr., the resistor temperature being approximately 2400 degrees Fahr. (1315 degrees Cent.).

DON MARQUIS :[3] I recently had occasion to run some tests similar to Mr. Tour's and I started out innocently enough to make my gas analysis, using a piece of $\frac{1}{8}$-inch steel pipe to sample the gas. I found by varying the size of the pipe and varying the flow out of the combustion chamber of my furnace that I got all kinds of variations in the analysis of the carbon monoxide and the carbon dioxide. It became apparent that I was not getting the true equilibrium of the furnace, but rather the equilibrium of the pipe in which I did my sampling.

[1]H. M. Heyn, "Atmospheres and Furnaces in the Wire Industry," *Wire and Wire Products,* October 1936, p. 507-520.

[2]Chief metallurgist, Hygrade Sylvania Corp., Emporium, Pa.

[3]Chief metallurgist of Detroit Plant, Thompson Products, Inc., Detroit.

I eliminated as much as possible of this variation by using a water-cooled pipe of stainless steel. I wondered how Mr. Tour coped with this difficulty.

JOHN E. WILKEY:[4] Mr. Tour is to be congratulated on his excellent paper. Had curves plotted from experimental data been included, it would have been more valuable in determining the equilibrium between carbon dioxide, carbon monoxide and water vapor. This data can be obtained either by absorption of the gas in P_2O_5 or by using a General Electric dew point potentiometer.

In the sampling of hot gases as questioned by Mr. Marquis, we find that reproducible results can be obtained by using a water-cooled quartz tube which eliminates the catalytic effect of nickel, chrome and stainless steel. This tube was developed by E. Mattocks, of the American Gas Association, and is described in report No. 748.

In the analysis of complex mixtures, it is advantageous to sample over mercury, as this does not affect water vapor content of the sample.

ASHLAND HENDERSON:[5] I am particularly interested in this question of water vapor about which Mr. Tour spoke at some length.

Early in the first paper, he mentioned the proposition that water vapor could not be determined with any accuracy in the mixture of gases that he was using, and later on calculated it in respect to propane. In the second paper, he mentioned that he removed the water vapor from the gas, and from a secondary reaction he drew curves showing the per cent of water vapor that was present.

I am wondering how he arrived at those figures in the first paper if there was no way to determine the water vapor present.

Author's Reply

This paper does not attempt to touch the field of the reactions between refractories, such as silicon carbide and reducing gases. Nothing in the paper offers a basis for an opinion on the question presented by W. E. Kingston.

The question presented by Mr. Marquis regarding reactions taking place in gas sampling tubes has been ably answered by the discussion offered by Mr. Wilkey. The problem of chilling a gas rapidly enough to stop reactions and changes in composition is serious. By using a water-cooled quartz tube such as referred to by Mr. Wilkey, an approach is made to the desired end. Whether or not this is a sufficiently rapid chilling to prevent gas reactions during the cool-down period is unknown. Both iron and nickel and possibly chromium are catalysts for the gas reactions involved. A stainless steel sampling tube might yield results differing from those obtained when using ordinary steel or nickel sampling tubes. Results obtained with one type of sampling tube and one sampling technique should not be compared with results obtained with another type of sampling tube or technique.

The suggestion by Mr. Wilkey that valuable data would be curves of actual water vapor determinations rather than calculations is agreed with. It is hoped that other experimenters in this field will make such determinations and present data.

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[4]Assistant chief chemist, The Cleveland Graphite Bronze Co., Cleveland.
[5]Metallurgist, Frigidaire Division, General Motors Corporation, Dayton, Ohio.

Mr. Gonser's supplying of the complete information as to the source of the "Heyn" curves is appreciated. His comment that the water of combustion is removed from the products of combustion from a commercial furnace atmosphere generator by the cooling of the gases in the condenser of the generator is quite to the point. This is a valuable attribute of certain commercial units.

Mr. Henderson's comment that "water vapor could not be determined" is based on a misunderstanding. The actual statement made was as follows— "While it is possible to determine . . . water vapor in furnace atmospheres, the fact remains that a majority of so-called . . . . . . analyses consist only of determinations . . . limited to oxygen, carbon dioxide and carbon monoxide. . . . The literature is almost wholly lacking in data regarding water vapor content of the atmospheres". Mr. Henderson's reference to the paper on "Furnace Atmosphere Generation" is also based on a misunderstanding. The actual statement was as follows—"Unfortunately, when this work was done, no direct determinations of water vapor content were made". The method of calculating the minimum water vapor present from the known products of combustion of a known gas is amply described in the paper. The fact that additional water vapor is formed on the reheating of the gases is evidenced by water condensation upon a second cooling of the gases. The amount of water vapor formed on reheating can be calculated from the decrease in hydrogen and the changes in CO and CO₂ resulting from the reheating or estimated roughly by the amount of condensation on a second cooling.

Professor Daasch warns "against conclusions too quickly drawn by abstract consideration" and proceeds to do exactly what he has warned against. In addition to drawing conclusions too quickly, Professor Daasch makes several erroneous statements as indicated below.

The speed of a reaction is governed by many things including temperature, presence of catalysts and mass action. In the cases of Reactions 3 and 5, the speed is also affected by turbulence of the gases and surface area and condition of the carbon. The general statement "The former is therefore the most important and effective reaction" is drawing conclusions too quickly even though Professor Daasch has preceded it by the statement "It is well known that _____."

However, whether the oxidation (not reduction as stated by Professor Daasch) of carbon is faster with CO₂ than with water vapor is immaterial to Reaction 1 which he questions as controlling. Reaction 1 does not involve carbon as such. It is entirely a gas reaction.

In connection with Reaction 1, Professor Daasch gives certain equilibrium values at 1600 degrees Fahr. (870 degrees Cent.) without any reference to source or authenticity. They seem to be greatly in error.

Reaction 1 is known as the water-gas reaction. There are no fixed equilibrium percentages for the various gases at any temperature. For a given temperature, the only thing that is fixed is the equilibrium constant (K) in the equation

$$K = \frac{P_{H_2} \times P_{CO_2}}{P_{H_2O} \times P_{CO}}$$

At the temperature of 1600 degrees Fahr. (870 degrees Cent.) chosen by Professor Daasch, the value of this constant K is approximately 0.843.

Substituting Professor Daasch's values in his Table A, we find an apparent equilibrium constant of 2.13 which is applicable for a temperature of about 1150 degrees Fahr. instead of 1600 degrees Fahr. (870 degrees Cent.). To be at true equilibrium at 1600 degrees Fahr. (870 degrees Cent.), Professor Daasch would have to change his CO to H_2O ratios or figures to approximately 45.4 per cent CO and 2.6 per cent H_2O. However, if he cared to, he could select any of the values as shown in the following table and still have equilibrium conditions at 1600 degrees Fahr. (870 degrees Cent.) for the water-gas reaction.

CO_2	H_2	CO	H_2O
2	50	45.4	2.6
2	50	2.6	45.4
5	45	43.8	6.2
45	5	6.3	43.8
10	40	37	13
40	10	13	37
10	20	66.5	3.5

It is quite obvious that Professor Daasch has made erroneous deductions "too quickly drawn by abstract consideration" of this individual reaction.

In his reference to Fig. 3, Professor Daasch seems somewhat confused. Fig. 3 is a representation of analyses of furnace atmospheres produced by the direct combustion of propane and air in a furnace. It is not an isolated equilibrium curve for the water-gas reaction.

Professor Daasch's comments regarding the speeds of the other reactions involved in studies of furnace gases are equally unsupported and possibly equally as erroneous.

THE TECHNIQUE OF MICRORADIOGRAPHY AND ITS APPLICATION TO METALS

By George L. Clark and William M. Shafer

Abstract

Since it is impossible to magnify X-ray images in the same sense that optical images are magnified by suitable lenses, it is necessary to register the X-ray image on a photographic plate and then enlarge the photographic image. By the use of the Lippmann emulsion with extremely fine grain size for the silver halide a magnification up to 200 may be made without loss of detail from graininess. Successful radiography also depends upon the choice of X-ray wave length which will give a maximum differentiation between constituents in a specimen such as aluminum and copper in an alloy. In this paper the theoretical absorption equations are developed leading to a simple and practical technique for metals. A careful study was made of photographic emulsions and developers. Instead of employing very soft X-rays at a few thousand volts with attendant prolonged exposure time very successful results were obtained with characteristic X-rays of molybdenum, copper and iron as produced in ordinary diffraction apparatus. A camera for multiple exposures is described and results are reported for copper-aluminum alloys, brass, type metal, and graphitic steel. It is demonstrated that supplementing the microscope, microradiography has great metallurgical usefulness with the advantages that it gives a three-dimensional view of a specimen, does not depend upon differential action of etchants but only on different absorbing power of constituents or inclusions, is directly and incontrovertibly interpreted, reveals internal voids and cracks, and requires no special polishing or preparation of the specimen. A semi-microradiographic technique for examination of very small welded pieces for soundness is also reported.

Introduction

RADIOGRAPHY is the oldest branch of X-ray science. Hitherto, it has been limited to the study of objects large enough to give radiographic images of sufficient size to be viewed by the unaided

eye. Obviously, it would be advantageous to obtain and view radiographic images of heterogeneous objects of very small size.

The purpose of this investigation was to develop a simple, rapid, microradiographic technique which could be applied to small heterogeneous bodies in metallurgical specimens. It was thought that such a method might be valuable in the study of alloys, welds, cracks, inclusions or any other inhomogeneities in metals. The radiographic images were correlated with microscopic images where possible.

HISTORICAL

Microradiography grew out of the desire to obtain and view radiographic images of heterogeneous objects of small size. As early as 1913, Goby,[1] using X-ray radiation of very long wavelength and working in a vacuum, obtained radiographs of fossils and minerals. These radiographs were then enlarged to such an extent that they could be viewed by the unaided eye. In 1930, Dauvillier[2] using a technique similar to that employed by Goby obtained radiographs of vegetable cells, such as those of elder pith. He used voltages as low as 8 kilovolts. The sample and photographic plate were both mounted in a vacuum connected directly to the X-ray tube in order to prevent absorption by the air of the low frequency radiation used. Lamarque[3, 4, 5] in 1936, using voltages of 5 kilovolts and currents as high as 100 milliamperes, studied plant and animal cells. The method was found very useful for studying the differences in densities of the various cell components.

This work on plant and animal materials led to the consideration of the application of a similar technique to the study of metallurgical specimens. The French Air Ministry[6] has employed a modified technique in the study of alloys used in the aviation industry.

THEORETICAL

The science of radiography is based upon the difference in absorption of X-rays by the various components of an inhomogeneous substance. The chief desire in a good radiograph is a maximum of contrast between the various components. For a given film, exposure

[1]P. Goby, *Compt. rend.*, Vol. 156, 1913, p. 686.
[2]A. Dauvillier, *Compt. rend.*, Vol. 191, 1930, p. 1287.
[3]M. P. Lamarque, *Compt. rend.*, Vol. 202, 1936, p. 684.
[4]M. P. Lamarque, *J. de Rad.*, Vol. 20, 1936, p. 6.
[5]M. P. Lamarque, *Presse Medicale*, Vol. 24, 1936.
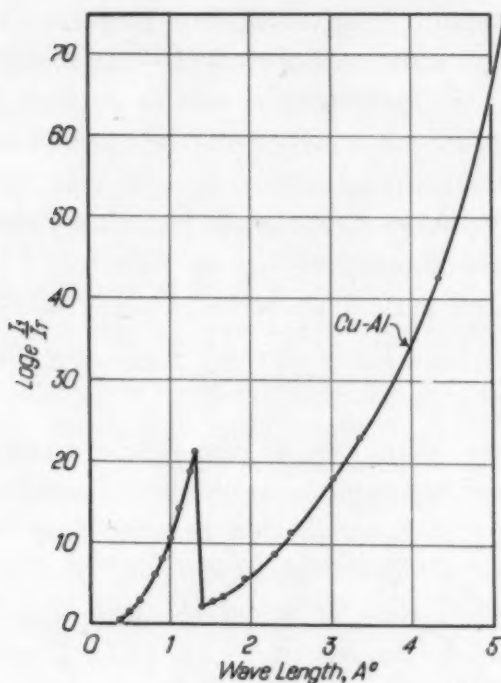[6]Private Communication, on visit by senior author in 1938.

Fig. 1—Graph of $\mathrm{Log}_e \dfrac{I_1}{I_t}$ as a Function of X-ray Wave Length for Copper-aluminum Alloys, Permitting Choice for Satisfactory Contrast on Radiograms.
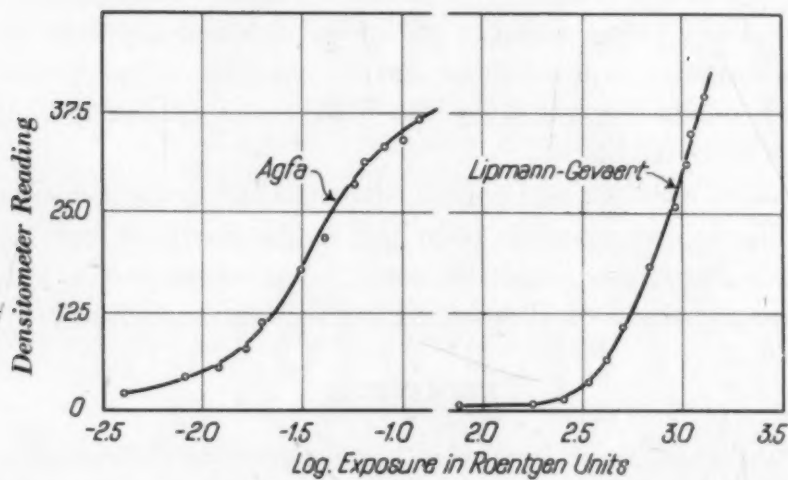

Fig. 2—Comparison of Photographic Characteristics for Agfa and Lipmann-Gevaert Films.

and sample, the contrast depends upon the mass absorption coefficients of the components which, in turn, depend upon the wavelength of the incident radiation.

In the following treatment, the effects of the thickness of sample,

thickness of component and wavelength upon the contrast have been worked out.

Consider a piece of metal consisting of two constituents with different mass absorption coefficients:

x_1 = thickness of component present in greater volume.
x_2 = thickness of component present in lesser volume.
I_0 = incident intensity of X-rays.
I_1 = intensity of X-rays after passing through component 1.
I_2 = intensity after passing through component 2.
I_t = intensity after passing through both components 1 and 2.

Then

$$(1) \quad I_1 = I_0 \, e^{-\frac{\mu_1}{\rho_1} \rho_1 x_1}$$

$$(2) \quad I_2 = I_0 \, e^{-\frac{\mu_2}{\rho_2} \rho_2 x_2}$$

where $\dfrac{\mu}{\rho}$ = mass absorption coefficient,

ρ = density

$$(3) \quad I_t = I_2 \, e^{-\frac{\mu_1}{\rho_1} (x_1 - x_2)}$$

$$= (I_0 \, e^{-\frac{\mu_2}{\rho_2} \rho_2 x_2} \, e^{-\frac{\mu_1}{\rho_1} \rho_1 (x_1 - x_2)}$$

$$(4) \quad = I_0 \, e^{\left[-\frac{\mu_2}{\rho_2} \rho_2 x_2 - \frac{\mu_1}{\rho_1} \rho_1 (x_1 - x_2) \right]}$$

From (1) and (4)

$$(5) \quad \frac{I_1}{I_t} = \frac{I_0 \, e^{-\frac{\mu_1}{\rho_1} \rho_1 x_1}}{I_0 \, e^{\left[-\frac{\mu_2}{\rho_2} \rho_2 x_2 - \frac{\mu_1}{\rho_1} \rho_1 (x_1 - x_2) \right]}}$$

$$(6) \quad \text{Simplifying} \quad \frac{I_1}{I_t} = e^{\left[\frac{\mu_2}{\rho_2} \rho_2 x_2 - \frac{\mu_1}{\rho_1} \rho_1 x_2 \right]}$$

The ratio $\dfrac{I_1}{I_t}$ determines the contrast between components 1 and 2. It is observed from equation (6) that $\dfrac{I_1}{I_t}$ is a function of the mass absorption coefficients, the density and x_2, but not x_1.

For the purpose of illustration, consider the case when constituent 2 is copper and constituent 1 is aluminum. This situation is
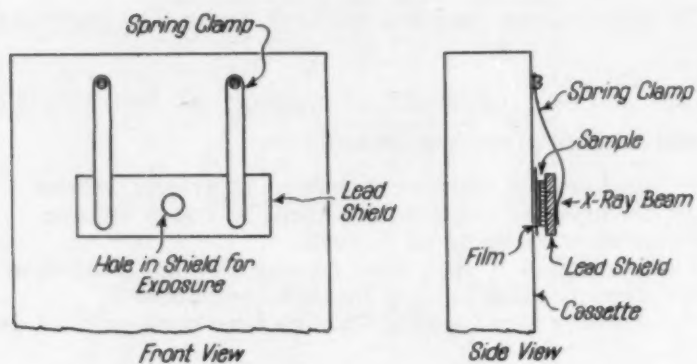
Fig. 3—Diagram of Simple Apparatus for Making Micro-radiograms.
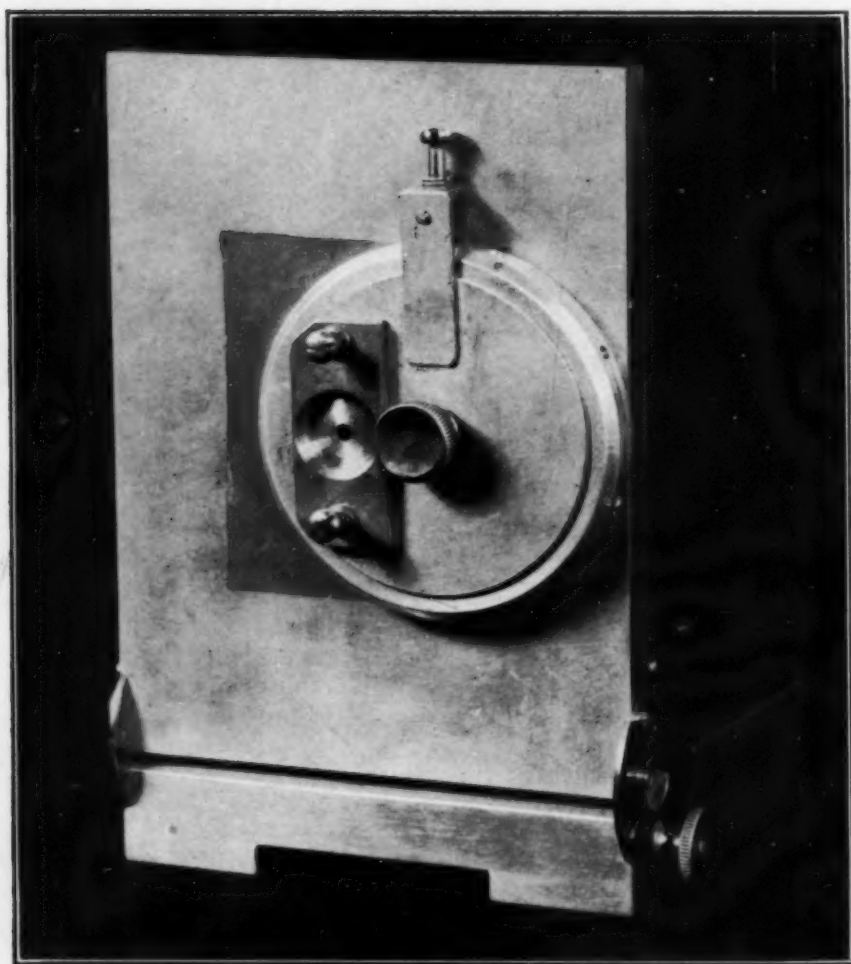
Fig. 4—Improved Microradiographic Camera.

met in the study of copper-aluminum alloys by microradiographic technique.

Let $x_2 = 0.01$ cm.

ρ_2 = density of copper = 8.50

ρ_1 = density of aluminum = 2.70

Then

$$(7) \quad \frac{I_1}{I_t} = e^{\left(\frac{\mu_2}{\rho_2} 8.50 \times 0.01 - \frac{\mu_1}{\rho_1} 2.70 \times 0.01\right)}$$

where $\dfrac{\mu_2}{\rho_2}$ = mass absorption coefficient of copper,

and $\dfrac{\mu_1}{\rho_1}$ = mass absorption coefficient of aluminum

From (7)

$$(8) \quad \text{Log}_e \frac{I_1}{I_t} = \frac{\mu_2}{\rho_2} (8.50 \times 0.01) - \frac{\mu_1}{\rho_1} (2.70 \times 0.01)$$

Now $\dfrac{\mu_2}{\rho_2}$ and $\dfrac{\mu_1}{\rho_1}$ vary with wavelength and may be found in handbooks.

By use of equation (8) the curve in Fig. 2 was obtained by plotting $\log_e \dfrac{I_1}{I_t}$ versus wavelength for copper and aluminum. A similar curve may be obtained for any two or more components. From such a curve, one observes how the contrast varies with wavelength and thus is aided in choosing a suitable wavelength.

In order to see how $\log_e \dfrac{I_1}{I_t}$ varies with x_2, again consider the copper-aluminum mixture using molybdenum $K\alpha$ radiation of 0.707Å. From equation (6)

$$(9) \quad \log \frac{I_1}{I_t} = \left(\frac{\mu_2}{\rho_2} 8.50 - \frac{\mu_1}{\rho_1} 2.70\right) x_2$$

From Fig. 1, $\log_e \dfrac{I_1}{I_t} = 4.2$ for a wavelength of 0.707Å and $x_2 = 0.01$ cm. Thus

$$(10) \quad \log_e \frac{I_1}{I_t} = 420 \, x_2, \text{ which is the equation of a straight line.}$$

From equation 10, the smallest value which x_2 may have and still be detected may be calculated. Also, the actual thickness of component 2 can be determined by measurement of I_1 and I_t.

EXPERIMENTAL

The principal points of the technique employed are:

1. The preparation of a sample in the form of a thin sheet 0.1 millimeter or less in thickness.

2.   The registration of the radiograph by a special technique.

3.   Enlargement of the radiograph to a suitable size.

The two chief difficulties encountered were: first, the obtaining of a photographic emulsion of sufficiently small grain size to stand enlargements of 100 and 200 diameters; and second, the obtaining of radiation of suitable wavelength and intensity.

1.   Study of Photographic Emulsions—Some experimental work was done on various photographic emulsions and developers. The photographic emulsions studied were Agfa non-screen X-ray film, Eastman fine-grain moving picture film, Eastman lantern slide emulsions, and Lipmann-Gevaert emulsions. The latter film is manufactured in Belgium. This emulsion is cast on a nitro-cellulose or cellulose acetate support and does not possess the characteristic opalescence of the ordinary radiographic emulsions. In order to study the grain size of the emulsions obtained by use of Eastman X-ray developer, enlargements of 110 diameters were made of each. These enlargements are shown in Figs. 5, 6, 7 and 8.

The fine-grain developers tried on the above emulsions were Sease No. 3, Doctor Parker No. 78, Champlains, and Odell's physical developer. No attempt was made to evaluate quantitatively the grain size of the emulsions under the various conditions of development.

In order to compare the Lipmann-Gevaert emulsion with ordinary Agfa X-ray film, the characteristic curves of each were constructed as shown in Fig. 2. A Victoreen r-Meter was used for measuring the intensity of radiation.

2.   Radiation—The problem of obtaining radiation of suitable wavelength and intensity is an important one. The marked increase in contrast obtained by the use of radiation of low frequency is obvious from Fig. 1. The short wavelength limit of the radiation is determined by the voltage applied. The wavelength moves towards longer wavelengths as the voltage decreases. Unless the atomic number of the target element is such that its characteristic emission radiation is excited by the applied voltage, the intensity of the radiation is low. In this work, the unfiltered radiations of molybdenum ($K\alpha_1 = 0.707\text{Å}$), copper ($K\alpha_1 = 1.54\text{Å}$) and iron ($K\alpha_1 = 1.93\text{Å}$) were used. Some work was done using voltages below that required to excite characteristic emission spectra but the time of exposure required was so long that low voltages were abandoned for the specimens studied.
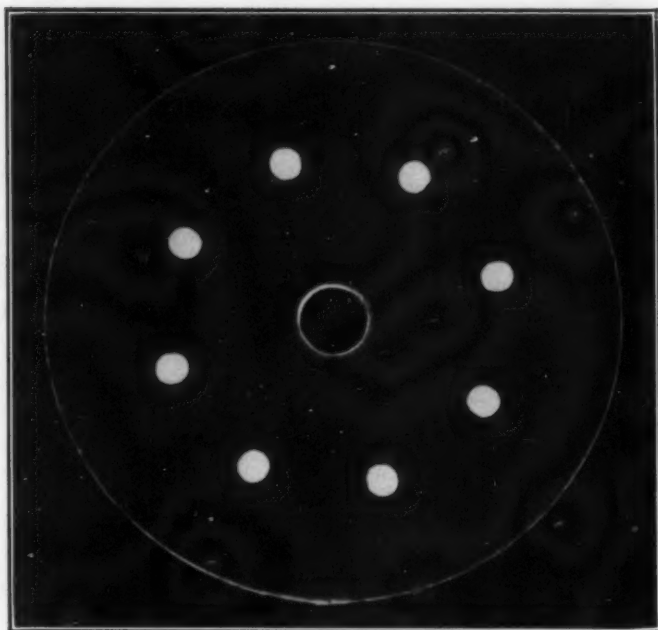
Fig. 5—Typical Radiogram.

3. Preparation of Samples—The samples were prepared in the form of thin sheets approximately 0.1 millimeter or less in thickness. Etching solutions, sand belts, emery paper or combinations of these were used in the thinning process. The final treatment was always with 2(0) emery paper. It was found that etching solutions generally left the surface pitted and that a final treatment with emery paper was necessary in order to remove the pits. The final treatment must be fine enough not to leave scratches sufficiently deep to show up in the radiograph. Samples were held during the thinning process on a flat metal surface by means of picein or Canada balsam. In cases where etching agents were used, the sample was mounted on a microscope slide.

4. Registration of Radiograms—Two different registration methods were used. The first method was to use the simple apparatus shown in Fig. 3. The sample was supported by means of Canada balsam or picein on a perforated lead shield. The relative positions of sample, emulsion, X-ray radiation and lead shield are shown in Fig. 3. In some cases radiograms were taken with the specimen placed directly against the emulsion and no paper between them. This seemed to give no observable improvement in definition, and it seemed that the emulsion was marked by the specimen in some cases.

An improved camera was designed and constructed as shown in
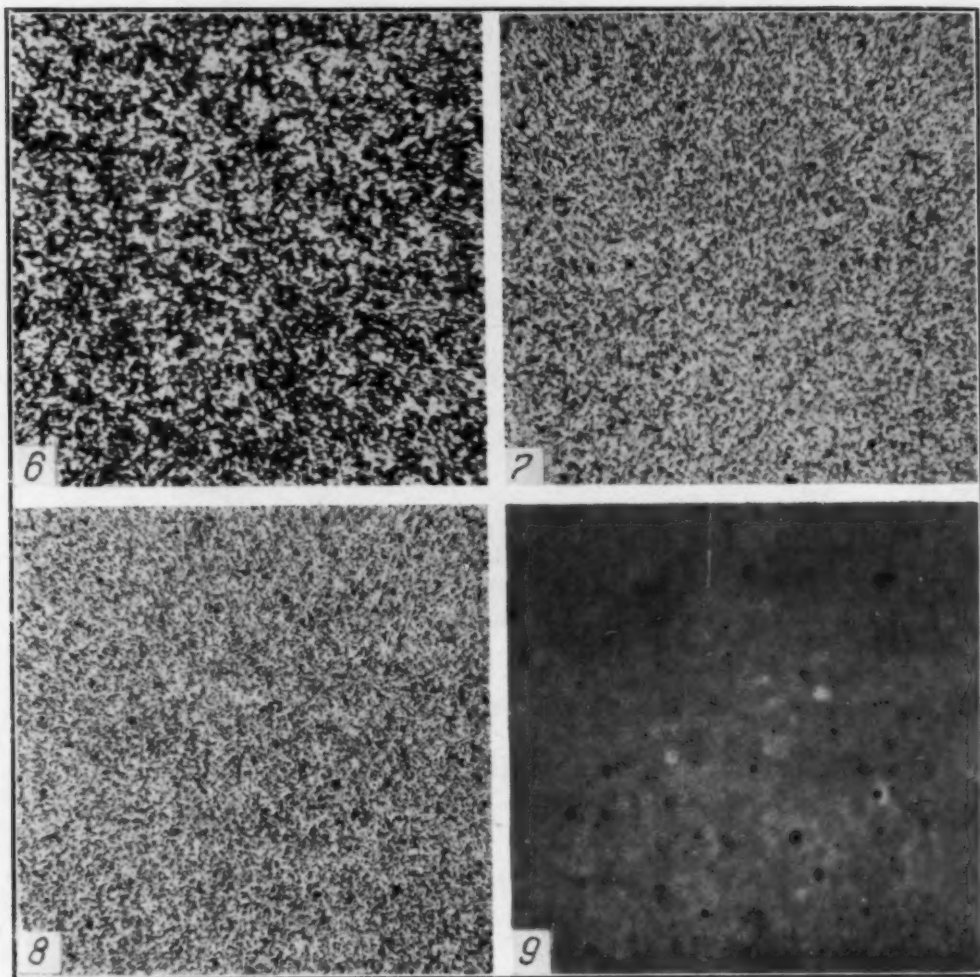
Fig. 6—Agfa Nonscreen. × 100.
Fig. 7—Eastman Lantern Slide. × 100.
Fig. 8—Eastman Moving Picture Film. × 100.
Fig. 9—Lipmann-Gevaert. × 100.

Fig. 4. This camera permits the registration of a large number of radiograms on the same film as shown in Fig. 5. By merely rotating the flat circular film holder, a new portion of film is exposed. The specimen is mounted on a perforated metal or glass slide of suitable dimensions by means of Canada balsam or picein and slipped into the slot prepared for it. The collimating tube with pinholes removed fits into the shallow, wide hole above the specimen.

5. *Enlargement of Radiograms*—The radiograms were enlarged to the magnification desired by the use of ordinary photomicrographic apparatus. The film with the radiogram on it was held flat by placing it between two microscope slides.
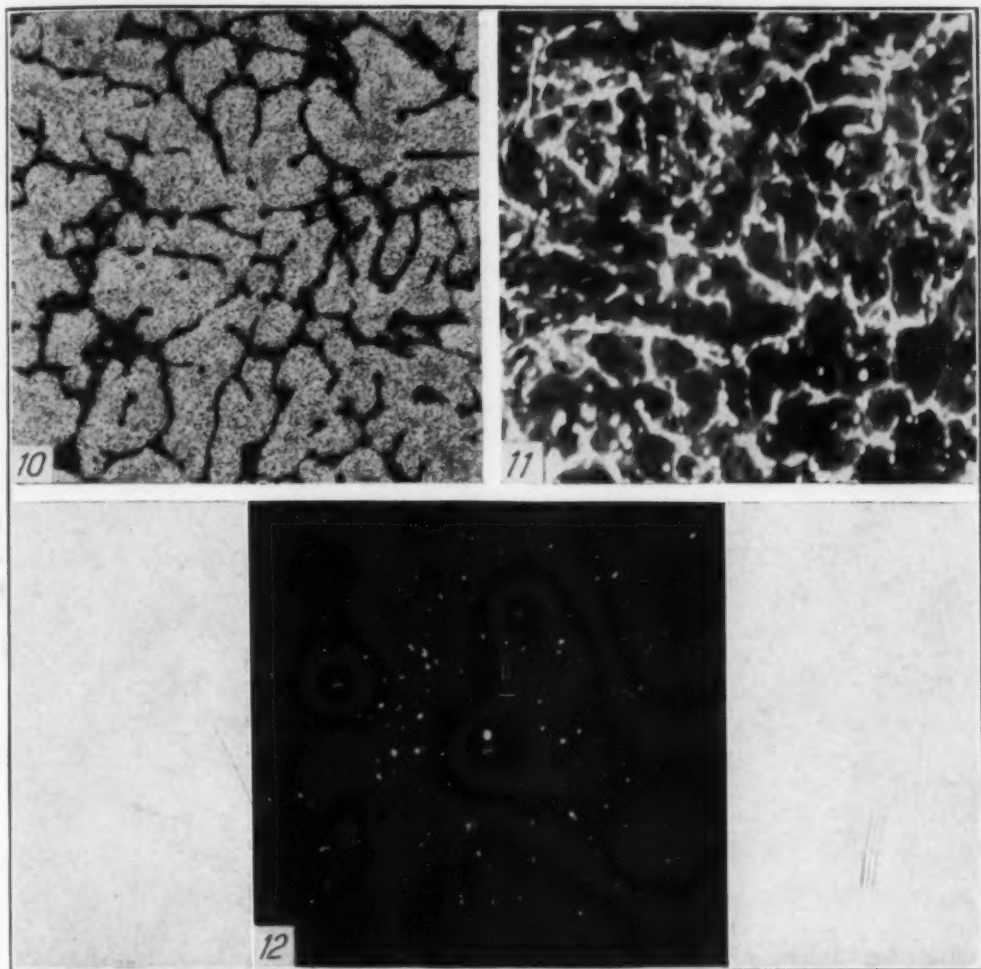
Fig. 10—Photomicrogram of Aluminum-Copper Alloy No. 1. CuAl₂—Black. Al—Gray. × 100.

Fig. 11—Microradiogram of Alloy No. 1. CuAl₂—Light. Al—Dark. × 100.

Fig. 12—Transmission Diffraction Pattern of Alloy No. 1. Some Elongated Laue Spots Indicate Strain.

6. *Study of Copper-Aluminum Alloys*—Photomicrograms, X-ray diffraction patterns, and microradiograms, shown in Figs. 10 to 18, inclusive, were made for each of three different copper-aluminum alloys. The specimens used for the diffraction patterns were etched from a thickness of 2.5 millimeters to a thickness of 0.6 millimeters. This severe etching was to remove any strained portions due to cutting. Transmission patterns were taken using molybdenum $K\alpha$ radiation and an exposure time of 1 hour at 15 milliamperes and 30 kilovolts.

The photomicrograms were prepared at a magnification of 100 diameters from specimens polished and etched according to A.S.T.M.
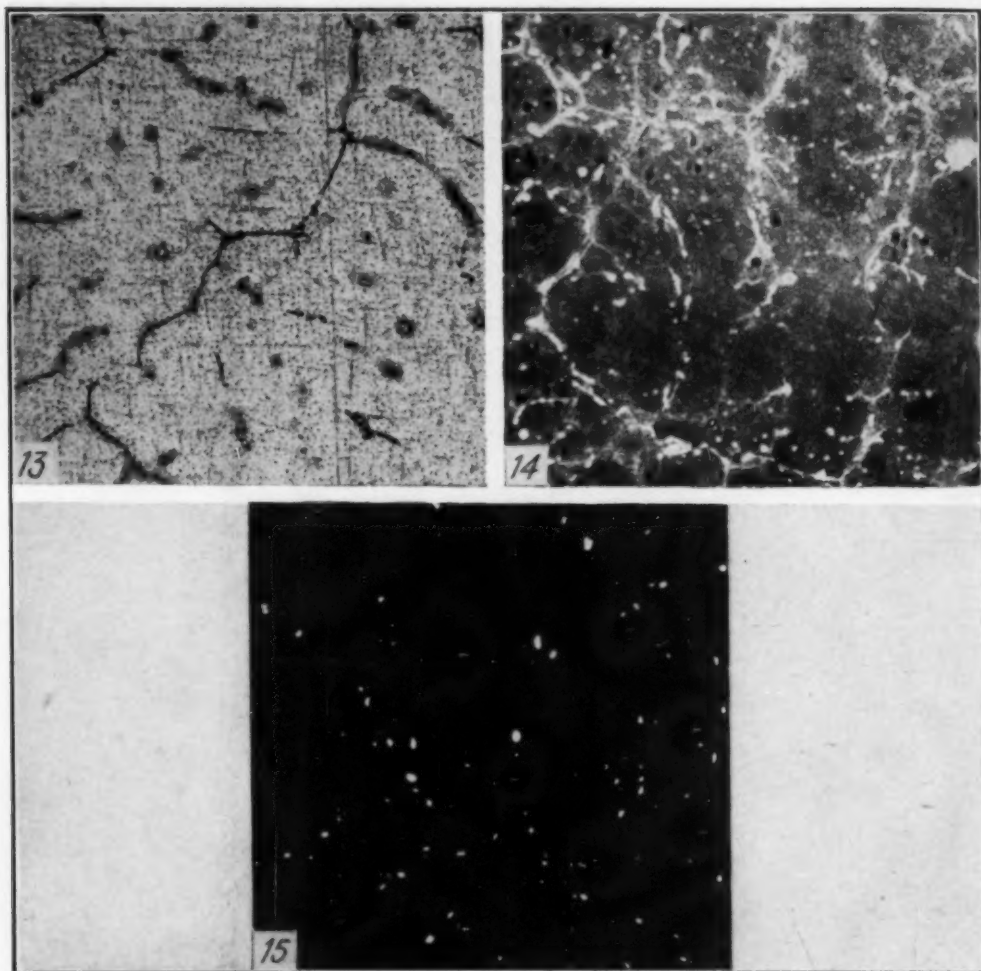
Fig. 13—Photomicrogram of Copper-Aluminum Alloy No. 2.   CuAl₂—Dark.   Al—Light.   × 100.
Fig. 14—Microradiogram of Alloy No. 2.   CuAl₂—Light.   Al—Dark.   × 100.
Fig. 15—Transmission Diffraction Pattern of Alloy No. 2.   Shows Almost No Strain.

specifications.   An etchant composed of 1 per cent hydrofluoric acid and 99 per cent water was applied for 20 to 30 seconds.

Microradiograms were prepared by the general technique described above.   The thickness of specimens was 0.05 millimeters, and the exposure time was 20 minutes.   Molybdenum polychromatic radiation, which was found to give greater contrast than copper radiation, was used.   The reason for this greater contrast is evident from the curve in Fig. 1.   It is observed from Fig. 1 that a wavelength of 0.707Å (no Ka) gives a larger value for $\log_e \dfrac{I_1}{I_t}$ than a wavelength of 1.54Å (CuKa).

7.   *Experiments with Brass*—Photomicrograms and microradio-
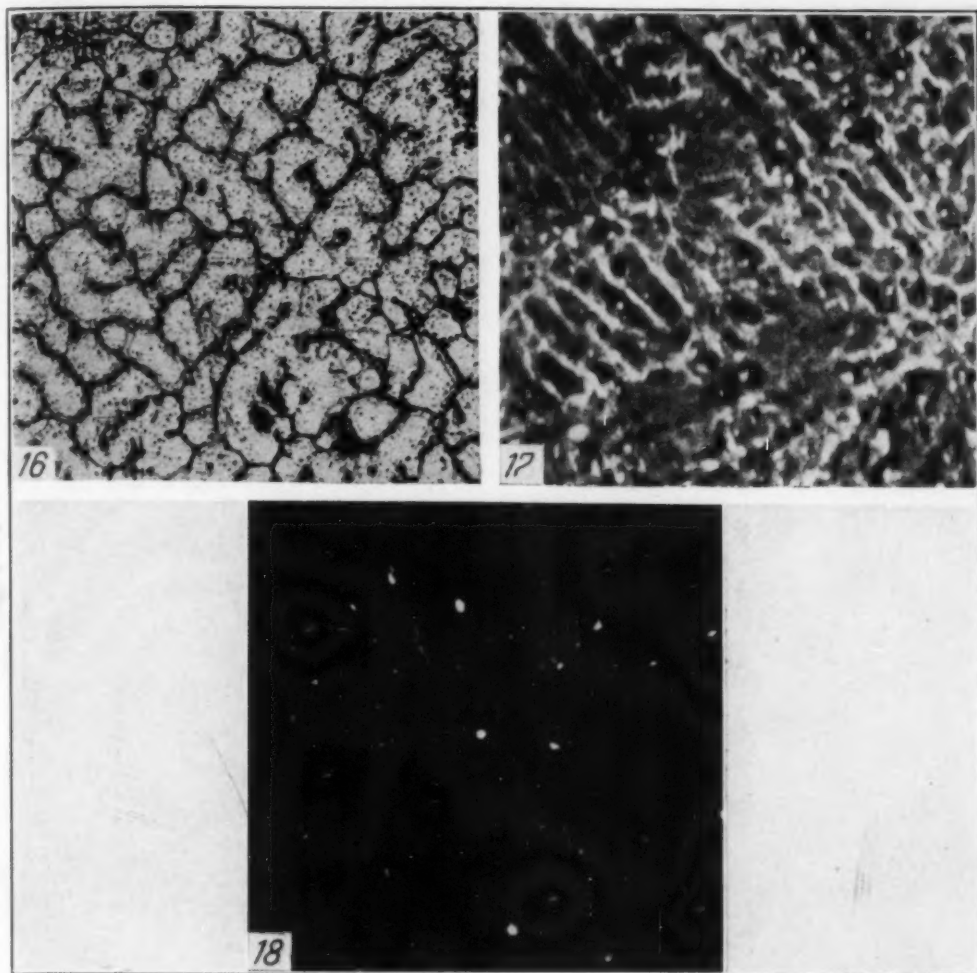
Fig. 16—Photomicrogram of Cu-Al Alloy No. 3.　$CuAl_2$—Dark.　Al—Light.　× 100.
Fig. 17—Microradiogram of Alloy No. 3.　$CuAl_2$—White.　Al—Dark.　× 100.
Fig. 18—Transmission Diffraction Pattern of Alloy No. 3.　Shows More Strain Than Other Two Alloys.

grams were prepared as shown in Figs. 19 to 23, inclusive. The composition of the brass, as stated by commercial analysis, was 60 to 63 per cent copper, 2.5 to 3.75 per cent lead, and the remainder zinc. The photomicrogram shown in Fig. 19 was obtained after polishing and etching with a solution of one part concentrated nitric acid to one part of water. The magnification is 100 diameters.

Polychromatic copper radiation was used to obtain the microradiograms. Exposures were approximately 2 hours for the thick specimens and 1 hour for the thin ones. Figs. 20 to 23, inclusive, show microradiograms of brass under the various conditions stated under the photographs.

8. *Microradiographic Study of Type Metal*—The thickness of
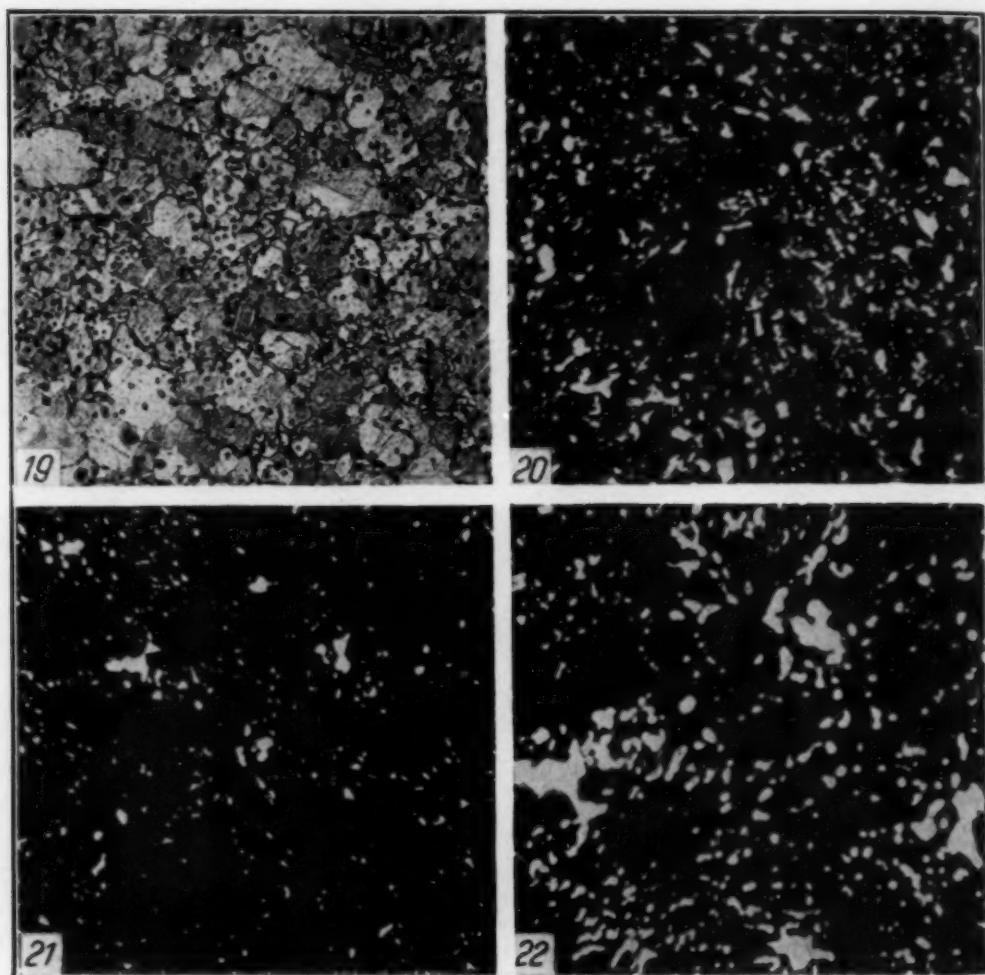
Fig. 19—Photomicrogram of Brass. Lead in Black. × 100.
Fig. 20—Microradiogram of Brass. Sample = 0.11 mm. Thick. Lead in White. × 100.
Fig. 21—Microradiogram, Sample = 0.06 mm. Thick. Lead in White. × 100.
Fig. 22—Microradiogram, Sample = 0.06 mm. Thick. Lead in White. × 200.

the specimens used was 0.04 millimeters. Because of the large amount of lead in these alloys, a long exposure of 3 hours using copper radiation at 20 milliamperes was required. The composition of the alloy shown in Fig. 24 is tin 8.50 per cent, antimony 12.85 per cent and the rest lead. Figs. 25 and 26 are microradiograms of a lead alloy containing 7.15 per cent tin and 13.40 per cent antimony.

9. *Application of Microradiographic Technique to the Study of Steel*—Fig 27 is a photomicrogram with a magnification of 250 diameters of one of the specimens of steel used, after being etched for 15 minutes with a 2 per cent solution of nital. The microradiograms at a magnification of 100 diameters are shown in Figs. 28
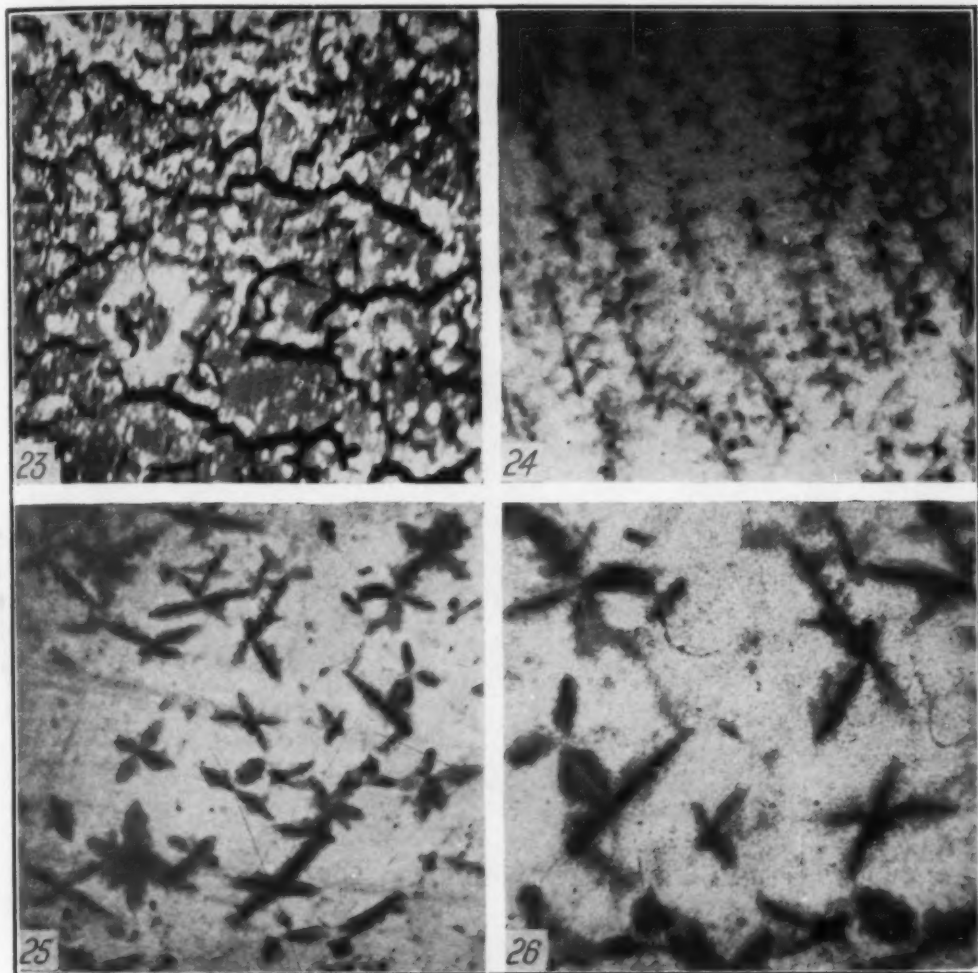
Fig. 23—Microradiogram of Brass, Showing Cracks. × 100.
Fig. 24—Microradiogram of Type Metal, Showing Sb-Sn Dark. × 100.
Fig. 25—Microradiogram of Another Type Metal Sb-Sn in Dark. × 100.
Fig. 26—Microradiogram of Same Alloy as Shown in Fig. 25.   Sb-Sn in Dark.
× 200.

and 29. The thickness of the specimens was 0.05 millimeters, and the exposure time was 30 minutes using 20 milliamperes and copper radiation.

10. A Semi-Microradiographic Technique Applied to the Study of Welds—What might be termed a semi-microradiographic technique was used in the study of some welds between alloys. The specimens were reduced to a thickness of approximately 0.30 millimeters on a sandbelt. Next, they were smoothed with 1(0) emery paper. The radiograms were registered by arranging the prepared specimens on a lantern slide plate covered by black paper as shown in Fig. 30. The plate and specimens were placed 50 centimeters
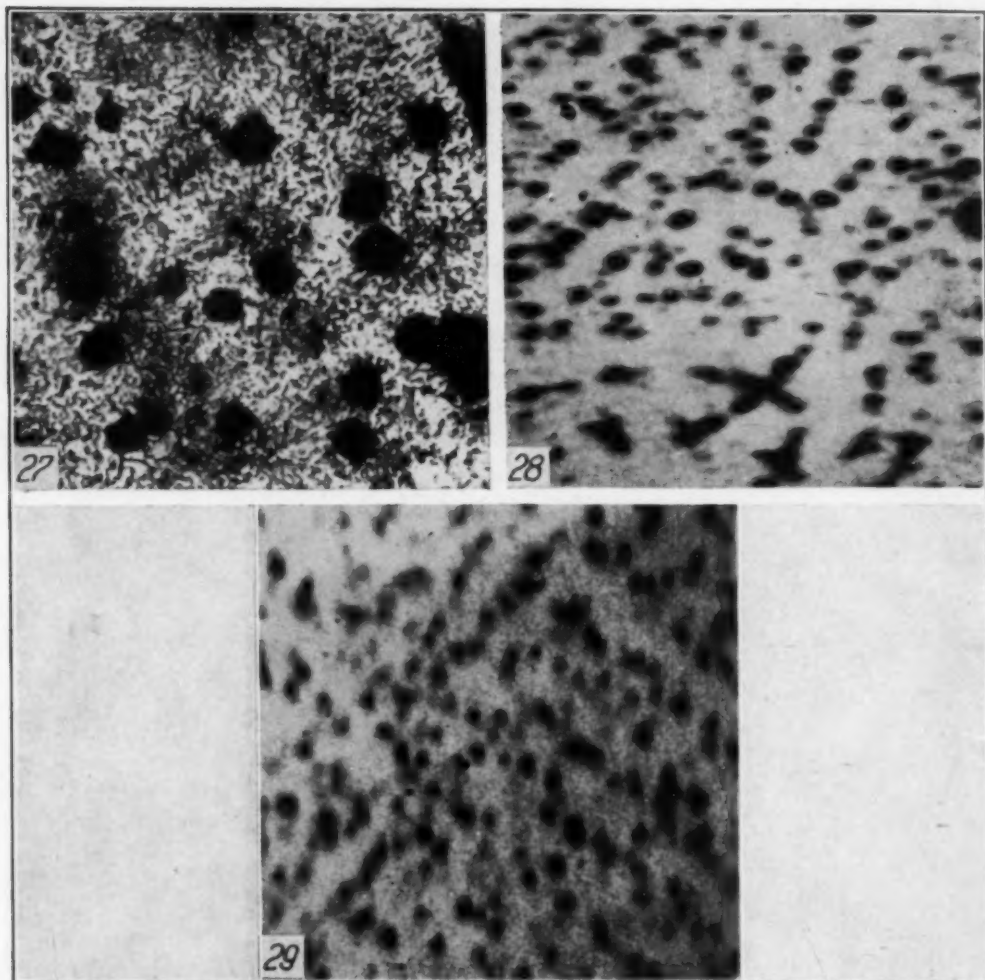
Fig. 27—Steel Sample No. 6.   Photomicrogram × 250.   Graphite in Black.   Pearlite in Gray.
Fig. 28—Steel Sample No. 6.   Radiomicrogram × 100.   Graphite in Black.   Pearlite in Gray.
Fig. 29—Steel Sample No. 4.   Radiomicrogram × 100.   Graphite in Black.   Pearlite in Gray.

from the target of a large radiographic X-ray tube.   The exposure was 30 seconds with the tube operating at three milliamperes and 175 kilovolts.

Photomicrographic equipment was used to enlarge the radiograms to 10 diameters.   Figs. 31 to 35, inclusive, show the enlarged radiograms.   The significance of the numbers in Fig. 30 are:

1.   Silver-molybdenum alloy welded to phosphor-bronze.
2.   Silver-graphite alloy welded to copper.
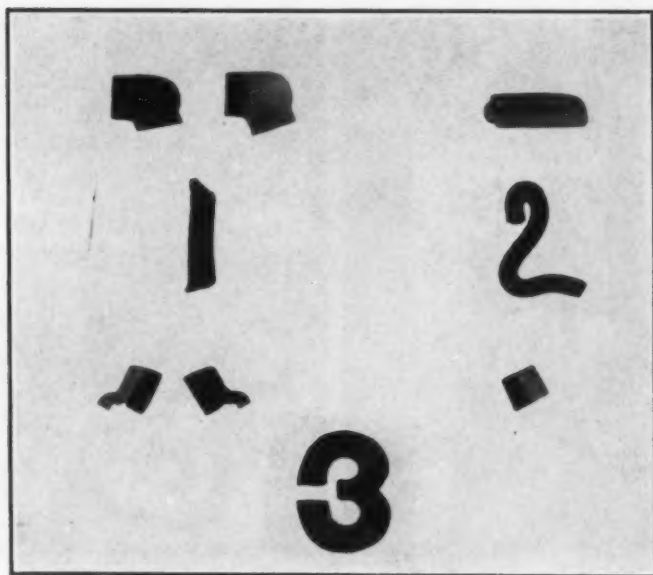3.   Silver-molybdenum alloy welded to bronze.
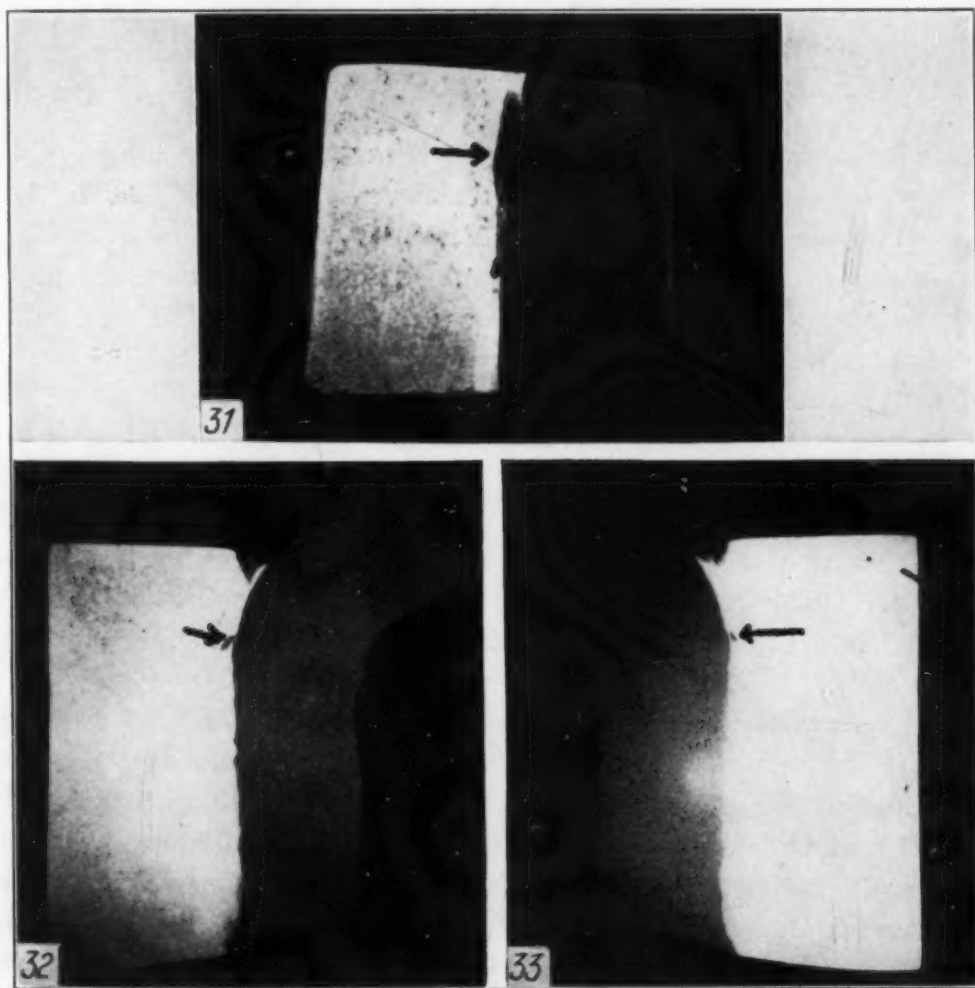
Fig. 30—Radiogram of Small Welded Pieces.   × 1.

Fig. 31—Radiogram × 10.   Arrow Shows Flaw in Weld.
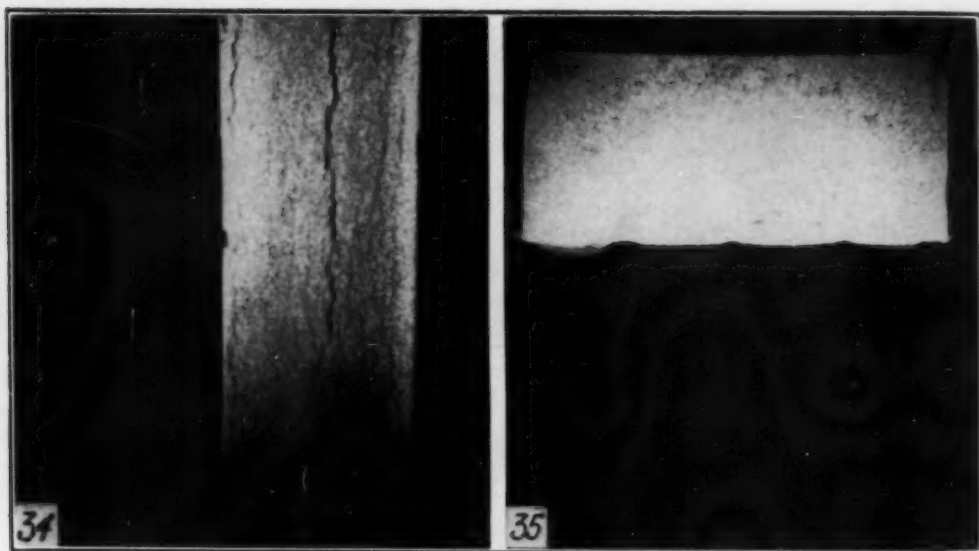Fig. 32—Radiogram × 10.   Arrow Shows Void.
Fig. 33—Radiogram × 10.   Arrow Shows Void.

Fig. 34—Radiogram × 10.　Shows Cracks.
Fig. 35—Radiogram × 10.　Shows No Flaws.

Discussion of Results

1.　Results of Experiments with Emulsions—The photographs of the exposed and developed emulsions when magnified to 100 diameters are shown in Figs. 6, 7, 8 and 9. The order of decreasing grain size is Agfa nonscreen, Eastman lantern slide, Eastman moving picture film, and Lipmann-Gevaert emulsion. The fine-grain developers were found to be more effective in reducing the graininess of fast, coarse-grain emulsions than in reducing the graininess of the slow, fine-grain Lipmann-Gevaert emulsion. There seemed to be no particular advantage in using the fine-grain developers on the Lipmann-Gevaert emulsion.

A study of Fig. 2 reveals the extreme slowness of the Lipmann-Gevaert emulsion. It is observed that the contrast above a density of 12.5 is greater for the Lipmann-Gevaert emulsion than for the Agfa.

2.　Results of Experiments on Aluminum-Copper Alloys—The microradiographic technique was found to be satisfactory for the examination of copper-aluminum alloys. The most satisfactory radiation is molybdenum or iron and not copper. The microradiograms give a three-dimensional view whereas the photomicrogram merely gives a two-dimensional view. The very dark regions in some of the microradiograms are probably due to voids and cracks which

become visible when magnified to 100 diameters. It must be borne in mind in comparing the microradiograms with the photomicrograms that the photomicrograms show only the $CuAl_2$ on the surface while the microradiograms show all the $CuAl_2$ in the region radiated.

It is interesting to compare the amount of strain manifested in the diffraction patterns of the various alloys with the amount of $CuAl_2$ present. Alloy number 2 has the least amount of $CuAl_2$ and the most strain. Alloy number 1 is intermediate in amount of $CuAl_2$ and in strain.

3. *Results of Experiments with Brass*—The lead shows up very distinctly in the microradiograms shown in Figs. 20, 21, 22 and 23. Figs. 20 and 21 show the effect of the thickness of sample upon the amount of lead appearing. This emphasizes the importance of knowing the thickness of specimen before comparisons of micro-radiograms are made. Fig. 22 is the same as Fig. 21 except that the magnification is 200 diameters instead of 100. This shows that good enlargements of 200 diameters may be obtained, without showing graininess. Fig. 23 shows the presence of cracks which may well be season cracks.

4. *Results of Microradiographic Study of Type Metal*—The microradiograms of type metal are shown in Figs. 24, 25 and 26. The dark crystals are probably an antimony-tin compound which solidifies first, and the matrix is the eutectic of antimony-tin and a solid solution of tin and antimony in lead. These antimony-tin crys-tals are the hard components in type metal which enable it to hold its shape. Here again, the microradiogram gives a three-dimensional view which shows the form and shape of the crystals and not merely a section such as the photomicrogram shows.

5. *Results of Application of Microradiographic Technique to Study of Steel*—The microradiograms shown in Figs. 28 and 29 show that graphite may easily be detected by this method.

6. *Results of the Semi-Microradiographic Technique Applied to Welds*—The results of this technique are very satisfactory. By this method inhomogeneities can be detected which could not be de-tected by any other method. The arrows in Figs. 31, 32 and 33 point to voids. Fig. 31 shows where the weld metal failed to flow and left a void. It is interesting to note that the voids in Figs. 32 and 33 appear at the same relative positions. Fig. 34 shows how readily cracks may be detected.

CONCLUSION

From a survey of this work, it is concluded that microradiography has a definite place in the study of metallurgical problems. It cannot supplant the microscope, but may well supplement it. Some of the advantages of the microradiographic method which may be pointed out are:

1. The microradiogram gives a three-dimensional view and not a two-dimensional one as obtained by a photomicrogram. This three-dimensional picture gives a better view of the shape of inhomogeneities.

2. The ability of a microscope to reveal the various components of a metal depends largely upon the differential action of an etchant. In some cases, as in the study of certain inclusions in steel, the inclusions are not differentiated by the etchant. Any substance which has a density differing appreciably from that of the matrix is visible in the radiogram.

3. The interpretation of the microradiogram is relatively simple. The substances with higher atomic numbers absorb the X-rays more strongly and appear as lighter spots on the radiogram.

4. Internal voids and cracks are perfectly visible in the microradiogram whereas they are invisible under the microscope.

5. Before a photomicrogram can be obtained, the surface must be highly polished. In the case of the softer metals and the ceramic materials, this polishing is a very difficult and time consuming process. The surface need not be highly polished in order to obtain radiograms.

One of the things which handicaps this microradiographic technique is the slowness of the Lipmann-Gevaert emulsion used. This seems to be a characteristic of all fine grain emulsions. The film is satisfactory from the standpoint of grain size. Certain imperfections appear in the emulsion which might be removed by more careful preparation of the emulsion.

DISCUSSION

Written Discussion: By Walter W. Offner, engineer, Industrial X-ray Laboratory, Seattle, Wash.

The author has developed an entirely new field for X-rays. There is no doubt that radiomicrography is of fundamental value to the metallurgist. The possibility of producing a three-dimensional picture, supplementing photomicrographs cannot be overrated. In many instances where the etchant cannot differentiate various metal components a radiomicrogram recording varying densities will solve the problem. Professor Clark's first announcement of his

research work on radiomicrography and its possibilities was so interesting that I inquired from various film manufacturers the possibilities of obtaining a fine-grained film for magnification. DuPont is producing a microfilm, however, so far I have not received any information as to its speed and grain size. Eastman Kodak Company replied that they are able to produce a fine-grained film similar to the Lippmann Gevaert film. Enlargements of 750 to 1000 times do not reveal any grain structure of objectionable size on this Eastman film. This extremely fine grain structure naturally necessitates long exposure times. Of course this Lippmann type emulsion has to be made on special order. Should anyone of these domestic films prove satisfactory, the import difficulties of the Lippmann Gevaert film might be avoided. It would be interesting to know if Professor Clark has tried this Eastman film and the DuPont microfilm and what his results were.

Written Discussion: By H. E. Seemann, physics department, Research Laboratories, Eastman Kodak Co., Rochester, N. Y.

The authors have presented an interesting application of microradiographic technique and one which demands considerable care. The microradiographs are excellent. Not being a metallurgist, this reviewer is not qualified to suggest applications in metallurgy but it would seem that revealing alloy structures by X-ray penetration would make a valuable supplement to the photomicrograph of the surface. The "semi-microradiographic technique" ought to be quite useful in welding research and has the advantage of requiring only readily available photographic emulsions.

The section entitled "Theoretical" contributes to an understanding of the idea of subject contrast but a diagrammatic sketch and a few additional notes might make it more readable.

Oral Discussion

J. D. Hanawalt:[7] I am sure that we are much indebted to Professor Clark for his pioneering experiments and his interesting discussion of this technique. Stimulated somewhat by Professor Clark's activity in the field of microradiography, we have been making a few experiments along this line. There are some unique features of the technique which one might expect to be particularly useful in certain cases.

We have endeavored to distinguish between iron and manganese segregations or precipitations in magnesium by use of their characteristic X-ray absorptions. If one has a magnesium specimen having both iron and manganese particles and makes a microradiograph using the radiation from a nickel anode X-ray tube, the iron particles should absorb strongly because the Ni $K\alpha$ 1.65Å radiation is short enough to excite the iron, whose K absorption begins at 1.74Å. For comparison with this microradiograph one would then produce another microradiograph using a cobalt anode X-ray tube. Since the Co $K\alpha$ radiation lies at 1.78Å it is too long to excite the iron K radiation and so would be transmitted by the iron but would be selectively absorbed by the manganese whose K absorption lies at 1.89Å. Thus, with respect to the manganese particles the iron particles should appear lighter in the first negative and darker in the second.

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[7] The Dow Chemical Co., Midland, Mich.

In practice we have not had any success with this experiment as yet, though we have only made a score of photographs, and there is undoubtedly a lot about the technique which we have not used in the most favorable way. One of the difficulties appears to be that the thickness of specimen which can be used must be about the order of magnitude of the size of the segregations, since the radiograph really gives one a great many two-dimensional views piled on top of each other rather than a three-dimensional view. Also, for the same small size of particle, the thinner the specimen the greater will be the contrast practically obtainable on the negative. If one has to work with thin specimens of one-hundredth of a mm. instead of a tenth mm., depending on the size of the particles he is looking for, specimen preparation becomes more difficult. Great care will be needed in preparing a specimen with very smooth, clean surfaces, and having no physical defects. These remarks are made for the purpose of indicating that practical difficulties may put some severe limitations on the applications of microradiography.

R. F. MEHL:[8] A paper such as this, which presents preliminary results of the application of a new method of investigation, suggests application to a host of other problems. The method is new and may well afford information on problems upon which other methods have not been very useful. Although the authors have doubtless considered many of these applications, it might be interesting and suggestive to list a few of them.

A question first: Can the method be applied stereoscopically, so that the orientation in three dimensions of geometrical shapes imbedded in a matrix could be determined? Present methods for the determination of such orientations are indirect, involving the measurement of angles formed by the shape with the surface of polish, and are time consuming; and occasionally they do not give unequivocal answers. This method, which finally conquers the problem of metal opacity for fine-scale studies, might well be important in such crystal orientation studies if it can be applied stereoscopically and if it can afford accurate results geometrically.

I might merely itemize a few problems upon which the method may provide interesting results. Could it detect carbide precipitation and chromium depletion at grain boundaries in stainless steel, in a more sensitive way than the microscope? Would it be of use in studying the early stages of precipitation in age-hardening alloys, about which there is so much controversy? Could it detect whether a metal diffuses at the grain boundaries of another metal more rapidly than within the grain, as for example copper in aluminum in Alclad where the heavy copper might give the requisite higher absorption? Would grain boundaries show up owing to a slightly lesser packing density? Since it has long been held, following Gibbs, that the solute in solid solutions is either more concentrated or less concentrated at the grain boundaries than within the grain, could this also be detected owing to differences in absorption?

C. NUSBAUM:[9] Would Professor Clark give us some idea how thick the samples were, between what limits?

Authors' Reply

I know of no one in the world that I would rather have try a method like this than Dr. Hanawalt, because his ideas and his technique and his conclusions can be, as always, absolutely depended upon.

I have no misgivings concerning some of the difficulties inherent in this method.

It does require still a great deal of practical testing with all sorts of specimens. There certainly is nothing wrong at all with the idea Dr. Hanawalt has for selectively bringing out the iron and manganese and I am hopeful enough to believe that with his keeping at it, the method will be successful. You may be sure, as I am, that a real test will be given to these problems in the Dow Laboratories. I am delighted that these attempts have been made, because they all contribute.

It is perfectly obvious we cannot expect this method to take the place of the microscope. It is not intended to do that. It is just a supplementary technique with the idea of gaining some types of information that we might not otherwise gain, and to that end it is worth, I think, the united effort of all of us. We need statistical experience before we know just where we can go. We did not go nearly far enough to know the limits of thickness and other details of technique, because so far it has been a matter of selecting materials and getting a start. I very much hope that these essential experiments of Dr. Hanawalt will turn out to be successful.

Now Dr. Mehl can think of more applications of new techniques than anybody else I know of, and so the problems that he has suggested present an inspiring challenge.

Yes, the stereoscopic method is decidedly possible and called for. We have only made one trial so far but we know that we can just as easily use the stereoscope as the physician does in his examination of radiographs of the chest or of kidney.

Now, of course, it is not possible for me to answer all of the problems which Dr. Mehl has submitted; I hope that he and the people under his direction will make these trials for detection of carbide deposition in stainless steels, diffusion of metals, and the matter of local concentration in solid solutions at grain boundaries.

I think we have evidence by this technique that that is a localization of the copper at the grain boundaries in aluminum alloys. I remember that the X-ray laboratory staff of the Air Ministry at Paris was very much concerned about some of the aircraft aluminum-copper alloys. The scientists were attempting to obtain radiographic results on thin metal specimens at 3000 or 4000 volts without very much success; nevertheless they have the keenest desire to answer that very question—is this a homogeneous alloy and what is happening to it? And I remember that Dr. Fournier told me that it was disclosed that the most unsuspected phenomena were developing at these grain boundaries.

So I hope that we may gain experience with these very important problems. We have tried some pure metals but we have never yet found a microradiograph that indicated an absolutely pure metal.

You understand, of course, that this method does not depend upon any kind of differential etching or special polishing or treatment of the specimen surface. The heavy metallic element, in accordance with well-known laws, absorbs the radiation for more than a light metal, except when we have the characteristic effects of which Dr. Hanawalt has spoken. This is a science all in itself, and therein, of course, lies one of the advantages of the method aside from the fact that we are actually passing a beam through a finite thickness rather than simply reflecting light from a surface. I think Dr. Hanawalt is right in saying that the microradiogram is probably one picture piled on top of another. We have only to prepare the photomicrograph and compare with the microradiograph to see just what the actual difference is.

Now we have not gone far enough to answer fully Dr. Nusbaum's question as to the limitation of thickness. We have gone from a millimeter on down to a hundredth of a millimeter. The equations developed in the paper as approximations, of course, are a function of X2, the thickness, in the path of the X-ray beam of the constituent of lesser volume. So that it may well be, particularly in certain combinations, we will get a definition and good results with an exceedingly thin specimen. Again we have found it is possible to get a piece of zinc entirely too thin. Of course, the upper limit of thickness is obviously the practical one of time exposure. Of course, there is a practical upper limit, too, in the ability to interpret what we see, as Dr. Hanawalt has indicated. You can't expect to find a trace of A under a mass of B. But, of course, the advantage in the technique and the apparatus we propose is a very good speed with a wave length which is provided in ordinary diffraction apparatus which easily penetrates the thickness of the material.

Again, as already intimated, the technique does not involve a matter of high polish but it does involve the matter of preparing a fairly smooth specimen; otherwise, the ridges and valleys and scratches will be obvious; but we have found 00 emery paper, carefully applied, is quite adequate for magnifications at least up to 200.

So most of these questions, then, involve further research. I hope everyone who has the simplest kind of apparatus—it is so easy to do—will try the method. Then we will put all our experiences together in another year or so and see if we can't have an American microradiography.

Since the presentation of this paper further progress has been made with the technique and applications of microradiography. The Eastman Kodak Company is now supplying a satisfactory Lippmann emulsion so that there is no longer need for concern that Belgian film is no longer available. Excellent results have been obtained on zinc containing lead in very small amounts; and especially with biological materials, such as tissues, wood, bone, etc. It has been possible to follow the path of nutrient fluids absorbed in fresh seeds, beans, etc., especially when a heavy metal ion such as lead, mercury or bismuth is dissolved in the fluid. It is gratifying that a method developed for metals should be adopted so easily to a wide variety of materials. It is the hope of the authors that the experiences of other laboratories with microradiography may be made known so that optimum experimental conditions can be established for the benefit of all.

EFFECT OF DEOXIDATION ON HARDENABILITY

By G. V. Cash, T. W. Merrill and R. L. Stephenson

Abstract

The hardenability was found to be a linear function of the grain size at the heat treating temperature, and the relation of hardenability to grain size was found to be independent of the method of deoxidation.

THE topic of grain size and its effect on hardenability is not a new one. In their original work on grain size, McQuaid and Ehn (1)[1] observed that fine grain steels showed more soft spots and therefore less hardenability than coarse grain steels. At the Grain Size Symposium of the American Society for Metals Convention of 1934, E. S. Davenport and E. C. Bain (2) pointed out that an increase in the austenitic grain size of a steel was accompanied by an increase in its hardenability. In a more recent publication, E. C. Bain (3) has measured the effect on hardenability of actual grain size differences and has compared these effects with the effects of various alloying elements. Besides these fairly quantitative treatments of the subject, there are also a large number of articles which recognize the difference in the hardenability of coarse and fine grain steels but show no quantitative measurements of the effect of grain size.

Unfortunately, from the steel producers' practice of classifying heats of steel as either coarse or fine by a grain size test run at 1700 degrees Fahr. (925 degrees Cent.), it has become a habit among investigators to separate their heats as coarse or fine by the same method and to lose sight of the fact that the austenitic grain size is a function of the temperature and consequently may cover a wide range. For this reason, it is highly misleading to assign one particular hardenability to a heat of steel since it may have any number of hardenabilities depending on the grain size at the temperature from which it is heat treated.

In this paper the authors present evidence which shows that the

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[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

hardenability of any steel is influenced by its austenitic grain size at the time of quenching and depends on the deoxidation practice only in that the deoxidation practice determines the temperature at which any given grain size can be produced. In other words, the hardenability is a linear function of the grain size alone and is in this sense independent of the different additions of aluminum that are made to control the McQuaid-Ehn grain size.

In order to obtain both coarse and fine grain steels for this investigation and at the same time eliminate as many other variables as possible, enough aluminum was added to one ingot of each of several coarse grain heats to make that ingot "fine grain" in the McQuaid-Ehn sense. In addition to the coarse and fine grain heats produced by deoxidation in the molds, two heats of matched analysis, one made coarse and the other fine by regular ladle deoxidation, were selected. The analysis and grain size of these heats are shown in Table I.

Table I
Chemical Analysis

	Deox.	C	Mn	Si	Al	Ni	Cr	Mo	McQuaid-Ehn Grain Size
Heat A	F.G.	0.79	0.62	0.21	0.058	....	....	....	3 - 5
	C.G.	0.78	0.63	0.23	0.008	....	....	....	2 - 4
Heat B	F.G.	0.55	0.76	0.18	0.028	....	....	....	6 - 8
	C.G.	0.56	0.76	0.18	0.003	....	....	....	1 - 3
Heat C	F.G.	0.43	0.71	0.19	0.062	....	....	....	6 - 8
	C.G.	0.46	0.71	0.19	0.003	....	....	....	1 - 3
Heat D	F.G.	0.41	0.86	0.20	0.031	0.01	0.06	0.01	6 - 8
Heat E	C.G.	0.43	0.85	0.20	0.006	0.01	0.05	0.02	1 - 3

The general heat treating procedure was maintained the same throughout the investigation so that comparable and reproducible results could be obtained. Cylindrical samples 1.5 inches in diameter were machined from the midpoints of large billets and heating was done in cast iron chips to prevent scaling or decarburization of the surface. Each piece was heated to a different temperature to produce the grain size peculiar to that temperature and after two hours was transferred to a salt bath so that the final quenching of every piece was from the same temperature. The quenching was done in water flowing with constant velocity through an upright cylinder, and the test pieces supported on wires, were held in the center of the cylinder by means of thin metal guides (Fig. 1). This pro-

cedure was found to effect very consistent results and maintained a
constant severity of quench during the experiment. (Severity of
quench was about H — 8.0).

After the samples had been quenched, they were notched and
fractured; one half was rated for fracture grain size while the other
was polished, etched and measured for hardness penetration. The
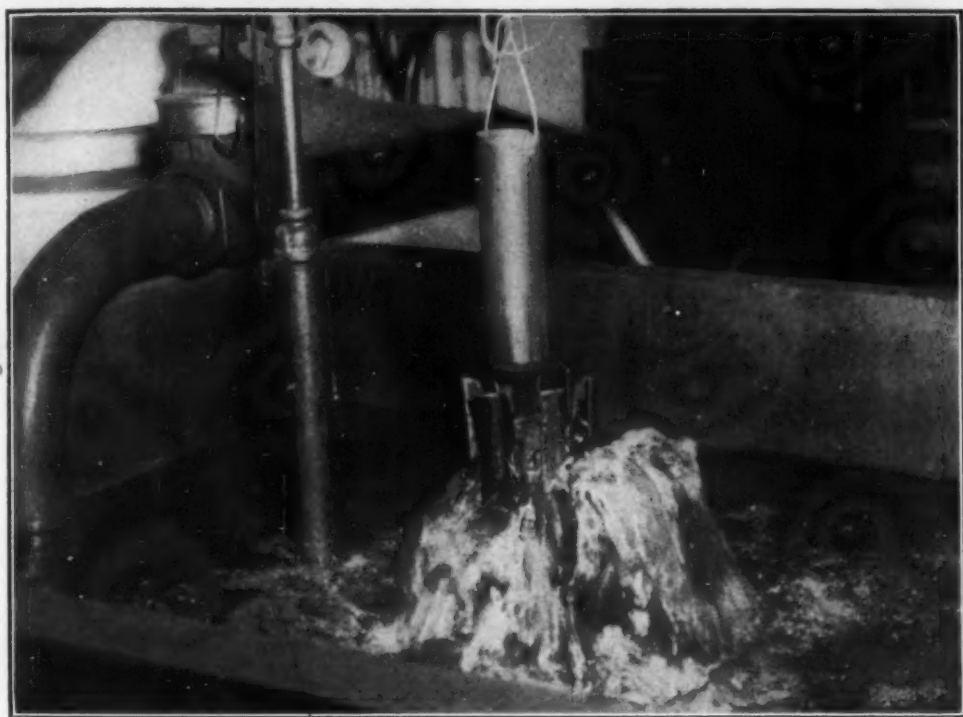fracture method was selected for rating the grain size since the

Fig. 1—Photograph of Fixture Used for Quenching Samples.

authors believed it to be more representative than an average of
microscopic ratings. With this method different observers were able
to check one another within a quarter of a grain size number except
in a few cases where duplexing was encountered. In such cases more
attention was paid to the microscopic ratings at the transition zone.
It is of interest to note here that in the few cases where duplexing or
mixed grains occurred, the coarse grains were found to harden more
deeply than the fine grains making the rating difficult, as exemplified
in Fig. 2.

For measuring the hardenability, the depth of hardness penetra-
tion to the point of 50 per cent pearlite was selected since it could be
determined easily both from the familiar hardness distribution curves
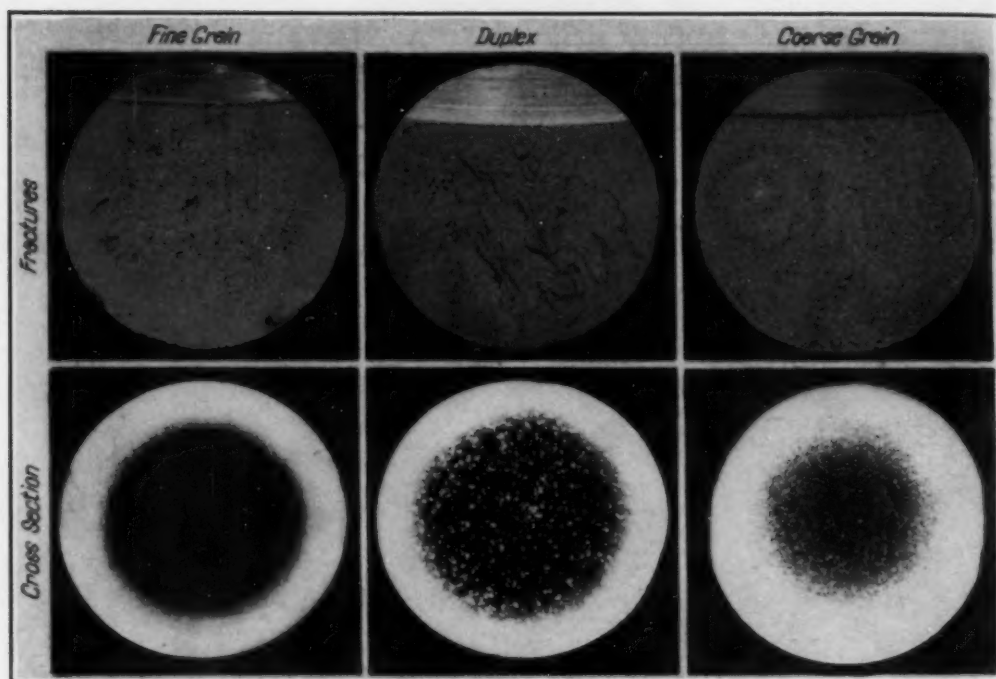
Fig. 2—Photograph of the Fractures and Etched Cross Sections of the Fine Grain, Duplex, and Coarse Grain Samples.
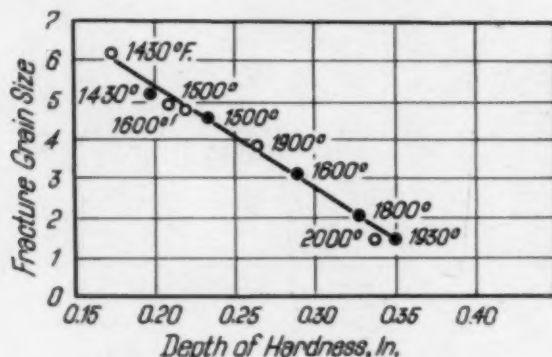

Fig. 3—Depth of Hardness Plotted Against Fracture Grain Size for Results Obtained from Samples from Heat A.

and even more accurately from microscopic measurements. The individual readings may be seen on the respective curves. Since the severity of quench was constant throughout, these results can readily be converted, if desired, to other measures of hardenability such as the ideal critical sizes suggested by Grossmann, Asimow and Urban (4). The results in terms of depth hardening, when plotted against the grain size, revealed that in the range of grain sizes investigated, the hardness penetration was substantially a straight line function. See Figs. 3, 4, 5 and 6.
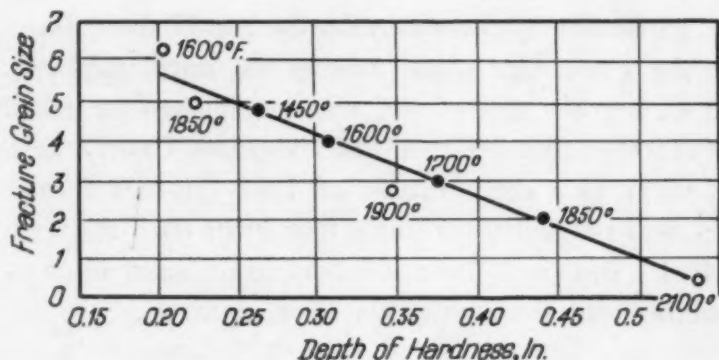
Fig. 4—Depth of Hardness Plotted Against Fracture Grain
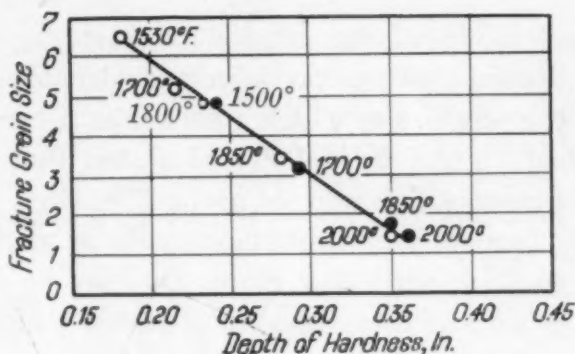Size for Results Obtained from Samples from Heat B.

Fig. 5—Depth of Hardness Plotted Against
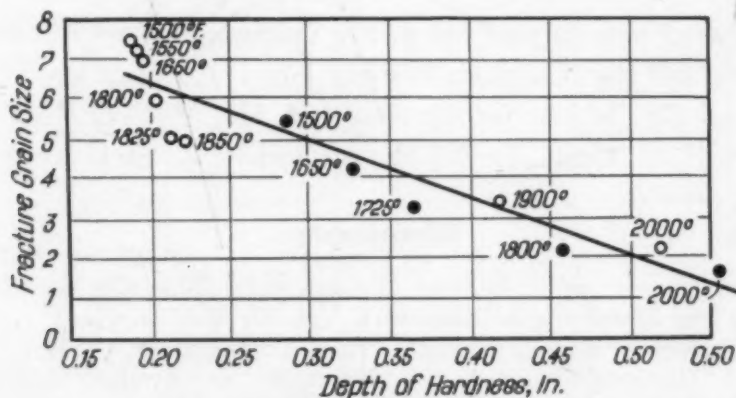Fracture Grain Size for Results Obtained from
Samples from Heat C.

Fig. 6—Depth of Hardness Plotted Against Fracture Grain
Size for Results Obtained from Samples from Heats D and E.

These lines furthermore indicate a striking relationship between
the "coarse grain" and "fine grain" steels. (Solid dots, coarse grain.
Hollow circles, fine grain). For any individual steel, the harden-
ability depends solely on the austenitic grain size established for
hardening, and is independent of the degree of deoxidation. As in-
dicated previously, the manner of deoxidation affects the temperature

at which a particular grain size may be established, but once it is established, the grain size alone affects the hardenability. Thus in Fig. 5, heat C, a grain size of 4¾ was established by a heating temperature of 1500 degrees Fahr. (815 degrees Cent.) in the coarse grain steel, whereas a temperature of 1800 degrees Fahr. (980 degrees Cent.) was needed to produce that grain size in the companion fine grain steel. But once these identical grain sizes were established, the hardenabilities of the two steels were identical.

SUMMARY

From consideration of the results of these experiments, it is evident that the deoxidation practice affects hardenability only insofar as it affects the temperature at which a particular austenite grain size may be established. The hardenability of a steel thus appears to be a function of its composition and its grain size when hardened, and the deoxidation practice is of importance only as it determines the temperature at which a particular grain size may be established, or as it affects the grain size established at a chosen temperature.

ACKNOWLEDGMENT

Bibliography

1. H. W. McQuaid and E. W. Ehn, *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 67, 1922, p. 341.
2. E. S. Davenport and E. C. Bain, "General Relations Between Grain Size and Hardenability and the Normality of Steels," TRANSACTIONS, American Society for Metals, Vol. 22, Dec. 1934.
3. E. C. Bain, "Functions of the Alloying Elements in Steel," a series of five lectures presented at the twenty-first National Metal Congress and Exposition, Oct. 1939.
4. M. A. Grossmann, M. Asimow and S. F. Urban, "Hardenability, Its Relation to Quenching and Some Quantitative Data," Symposium, Hardenability of Alloy Steels, American Society for Metals, 1939, p. 124.

DISCUSSION

Written Discussion: By B. R. Queneau, Lt. U.S.N.R., U. S. Naval Proving Ground, Dahlgren, Va.

The authors state that, within the range of grain sizes investigated, the hardness penetration is substantially a straight line function of the austenitic grain size. Grossmann and Stephenson in another paper being presented at this convention show that the linear relation is not between grain size and depth of case but rather between grain size and hardenability as measured by the square of the ideal critical size. When the ratio of depth of hardened case to the diameter of quenched round is small, a change in depth is roughly proportional to the change in hardenability. But when the ratio is large, a small change in hardenability will result in a large change in depth of penetration. If smaller rounds had been used in the experiment, no confusion between penetration and hardenability would have occurred since a straight line would have been obtained on plotting penetration versus grain size.

It might be well to point out that the word "deoxidation", as used by the authors, apparently refers only to aluminum additions; and furthermore, in all but one case, their fine-grained steels were made by adding aluminum to a coarse-grained heat in the mold. In the one case where a regular fine-grained heat was compared with a coarse-grained heat of similar composition, the hard-
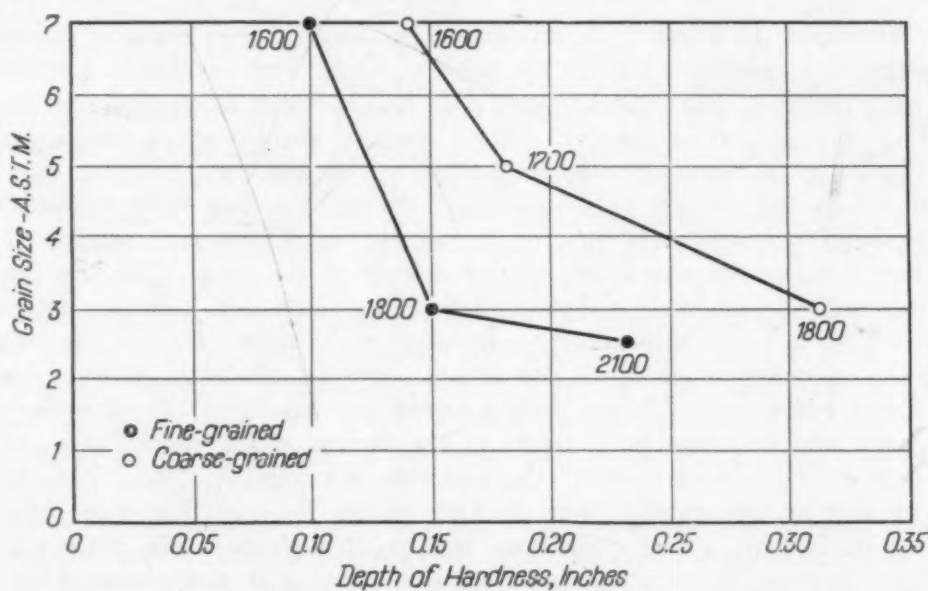

Fig. 1

enability was not independent of deoxidation practice. For instance Heat D (fine grain) had a case of 0.22 inch with a fracture grain size of 5. Heat E (coarse grain) with a somewhat finer grain size developed a case of 0.28 inch—a difference of $\frac{1}{16}$ inch.

The depth of case in rounds of Heat D when heated to 1900 and 2000 degrees Fahr. make it appear that both heats do have the same hardenability for a given grain size. Was a mixed grain size developed in steel D at these temperatures, and if so, what method was used to obtain an average grain size?

A few hardenability tests were made in our own laboratory to check the effect of deoxidation practice. One-inch rounds three inches long were machined from two bars, one fine-grained and the other coarse-grained, having substantially the same composition. The samples were heated in an electric furnace, held approximately 30 minutes at temperature and quenched into brine. Grain size and depth of case were measured under the microscope. The results obtained are shown in Fig. 1. Analyses were as follows:

	C	Mn	Si	Ni	Cr	Al
F. G.	1.08	0.23	0.08	0.03	0.12	0.015
C. G.	1.03	0.23	0.16	0.10	0.06	0.001

Only the fine-grained steel heated to 1800 degrees Fahr. showed a mixed grain size (65 per cent 1-2 and 35 per cent 6). It will be seen that the fine-grained steel heated to 2100 degrees Fahr. had a penetration of 0.23 inch, while the coarse-grained steel with a somewhat finer grain size had a penetration of 0.31 inch.

In this case at least, the deoxidation practice had a definite effect on hardenability as well as on grain size.

Oral Discussion

FREDERICK C. HULL:[1] In this paper the authors used depth of hardness penetration in quenched bars to the point of 50 per cent pearlite as a measure of hardenability. Hardenability may also be expressed by critical size round and critical quenching velocity. These various quantities are an indication of the ability of the steel to be fully hardened by a quench, and they are determined by the position of the cooling S-curve. For two steels to have the same depth of hardness penetration to the point of 50 per cent pearlite, their cooling S-curves must coincide in the vicinity of the knee. The method of Grange and Kiefer[2] could be applied to obtain the isothermal S-curves and these also would be found to be nearly coincident at the knee. It does not follow, however, that the curves would superimpose over the whole temperature range.

Mehl and Johnson [3, 4] have made a careful analysis of the rate of isothermal decomposition of austenite in terms of the factors which control this rate—grain size (a), rate of growth (G), and rate of nucleation (N). They have shown that at temperatures near the knee of the S-Curve, where the rate of nucleation is high, a further increase in rate of nucleation will produce only a slight increase in reaction rate or a slight decrease in time required for 50 per cent transformation. The explanation of this behavior is simple. When N is very great, the time required for the grain boundaries to be completely

[1] Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh.

[2] R. A. Grange and J. M. Kiefer, "Transformation of Austenite on Continuous Cooling and its Relation to Transformation at Constant Temperature," TRANSACTIONS, American Society for Metals, Vol. 29, 1941, p. 85.

[3] R. F. Mehl, "The Physics of Hardenability," Symposium, The Hardenability of Alloy Steels, published by American Society for Metals, 1938.

[4] W. A. Johnson and R. F. Mehl. "Reaction Kinetics in Processes of Nucleation and Growth," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 135, 1939, p. 416.

outlined is a small fraction of the time needed for the complete transformation of the grain. The rate of the subsequent transformation, which takes place by the growth inward of the pearlite nucleated at the boundary, is relatively insensitive to the rate of nucleation, as long as N is large. If nuclei formed within the grains, as they appear to do in some cases, this simplified picture would have to be modified.

When isothermal transformations are carried out above the knee and, in particular, near the critical range, the rate of nucleation has a marked influence on the rate of reaction. I believe that if the authors had performed experiments of this nature they would have found that the steel of fine McQuaid-Ehn grain size was faster reacting than the coarse-grained steel, even though they had been heat treated so as to produce the same grain size. Herty[5] studied the effect of deoxidation on the rate of formation of ferrite in hypoeutectoid steels and found that in steels coarsened to produce identical grain sizes the originally fine-grained steel was faster reacting than the originally coarse-grained one. He attributed this increased rate to the presence of fine particles which acted as nuclei for ferrite formation.

I merely wish to point out the fact that similar behavior may be encountered in the authors' steels, and that quenching experiments do not yield information about the relative rates of transformation in two similar steels at constant temperatures near the critical.

Authors' Reply

In his discussion, Dr. Queneau pointed out that straight line relation does not necessarily exist as we have shown between the depth of hardness penetration and the grain size, but the straight line relation does exist between the square of the ideal critical size and the grain size. In the examples we selected, however, the square of the ideal critical size was practically a straight line function of the depth of hardness penetration and so no error was introduced in this way.

Measurement of grain size was difficult at temperatures where duplexing occurred and Dr. Queneau pointed out this fact in his own work. The difference in hardness penetration which he shows for the same austenite grain size may be explained by the difference in residual alloying elements as silicon, nickel and chromium in his two heats, in the one case a total of 23 points and in the other 32.

Mr. Hull pointed out in his discussion that although fine- and coarse-grained heats are heat treated to produce the same austenitic grain size, nucleation in the heat of fine McQuaid-Ehn grain size may be accelerated by fine particles within the grains and in that way decrease the actual hardness penetration of the fine-grained heat below that of the coarse-grained heat. In the authors' experiments this was not found to be the case except when extremely coarse grains were produced; then nucleation did occur not only at the grain boundaries but also within the grains themselves and caused a corresponding decrease in the depth of hardness penetration.

[5]C. H. Herty, Jr., "Effect of Deoxidation on Some Properties of Steel," TRANSACTIONS, American Society for Metals, Vol. 23, 1935, p. 113.

EFFECT OF NITROGEN ON THE CASE HARDNESS OF TWO ALLOY STEELS

By S. W. Poole

Abstract

A study has been made of the effect of nitrogen on the case hardness of two case hardened medium carbon alloy steels after drawing in a temperature range of 300 to 600 degrees Fahr. (150 to 315 degrees Cent.).

It was found that with a medium carbon nickel-chromium steel the effect of the nitrogen content is to inhibit the softening effect on the case upon drawing in this temperature range. This effect was also indicated with a carbon-chromium steel.

It was found that a sodium cyanide bath gave the best results insofar as high surface case hardness is concerned.

The carbon-chromium steel was found to be generally superior to the nickel-chromium steel so far as maximum surface case hardness is concerned.

A metallographic study revealed several interesting features concerned with the type of case structure formed and the formation of a carbide skin at the extreme surface of the case.

T HIS investigation proposes to show the effect of nitrogen on the case hardness of nickel-chromium and carbon-chromium steel of medium carbon content after treatment in various commercial liquid case hardening baths followed by oil quenching and drawing. The types of commercial case hardening baths used will result in varying amounts of nitrogen being introduced into the case formed depending on the type of bath used and length of time of treatment in the bath prior to quenching.

The two steels used in this investigation, namely, medium carbon nickel-chromium and carbon-chromium steel, are both used in the manufacture of automotive gears which fact necessarily imposes certain metallurgical requirements upon this material. Of major importance is the factor of inherent grain size and the ability to form

a hard, wear resisting tooth surface when suitably case hardened. In case hardening transmission gears it is usual to harden a medium carbon alloy steel by means of a cyanide or other case hardening bath at approximately 1500 degrees Fahr. (815 degrees Cent.).

The inherent grain size is of importance due to its effect on the amount of distortion developed during quenching and its influence on the amount of retained austenite in the case after quenching. In this respect the type of case hardening bath used also has an effect on the amount of retained austenite.

It is a well known fact that an inherently coarse grain steel will produce a coarse martensitic case structure which is inferior in actual service performance to the fine dense martensitic case produced by a fine-grained type. A coarse and fine-grained type of steel were used in this investigation and effects on case structure are studied.

An important requirement insofar as gear performance is concerned is that the case hardness below the surface, for example, 0.010 inch or 0.015 inch from the surface, is of relatively less importance than the case hardness in the first 0.005 of an inch. This is an important consideration because in the modern rigidly mounted transmission made from gears which are very accurately cut and matched, wear of a few thousandths of an inch will affect the performance adversely. In this respect it is apparent that the formation of excessive retained austenite or the possibility of slight surface decarburization are serious factors making for poor performance.

Experimental Procedure

In conducting this investigation the following material was used:

(1) Steel in the form of 1.5-inch rounds was treated for the purpose of machining off successive layers from the carburized surface in order to determine the carbon and nitrogen gradation through the case. In preparing this material for treatment, ⅛ inch was turned from the diameter of 6-inch lengths for the purpose of removing any decarburization. A $\frac{1}{16}$ inch hole was then drilled transversely ⅛ inch from one end of each bar in order to suspend the sample in a case hardening bath.

(2) Samples for hardness determinations were in form of ½-inch rounds, 0.125 inch was milled from the diameter on opposite sides, thus producing two flat parallel surfaces for hardness readings. These milled sections were then cut into 2-inch lengths and $\frac{1}{16}$ inch

diameter holes were drilled transversely through each sample at a distance of ⅛ inch from one end. The parallel surfaces were then polished on No. 1-G emery paper to remove machining marks.

Data relative to the chemical composition and inherent grain size of the steels used is shown in Table I:

Table I

Large diameter (1.5-inch) rounds—Carbon-Nitrogen Checks.——

Steel		C	Mn	Ni	Cr	McQuaid-Ehn
Carbon-chromium		0.47	0.80	....	1.00	7-6 normal
Nickel-chromium		0.415	0.75	1.30	0.71	6-7 normal

Small diameter (0.5-inch) rounds—Hardness Determinations.——

Steel	Bar No.	C	Mn	Ni	Cr	McQuaid-Ehn
Carbon-chromium	1	0.505	0.70	....	0.94	7, some 4
Carbon-chromium	2	0.499	0.77	....	0.99	7, some 4
Carbon-chromium	3	0.440	0.73	....	0.96	7, some 3, 4
Carbon-chromium	4	0.470	0.78	....	1.00	7, some 4
Nickel-chromium	1	0.316	0.70	1.24	0.56	3-4
Nickel-chromium	2	0.310	0.69	1.24	0.59	3-4
Nickel-chromium	3	0.310	0.72	1.25	0.57	2-4
Nickel-chromium	4	0.300	0.74	1.25	0.58	3-4

The samples prepared for determination of the carbon and nitrogen gradation and hardness were treated in a series of commercial hardening baths with the exception of one group of samples which was pack carburized. These baths are designated as follows:

(1) Bath No. 1—Activated type.
(2) Bath No. 2 (33 per cent sodium cyanide)—Straight cyanide type.
(3) Bath No. 3—Carburizing type bath.
(4) Bath No. 4—Activated type (Calcium cyanamid).
(5) Bath No. 5—(Solid "pill" type carburizer).

The composition of the solid carburizer is:

Hardwood charcoal ....71 per cent
Barium carbonate ....10 per cent
Calcium carbonate .... 5 per cent
Sodium carbonate .... 2 per cent
Oil (S.A.E. No. 20 grade) ......12 per cent

Baths No. 1, 2 and 4 will introduce considerable quantities of nitrogen into the case besides carbon. Bath No. 3 and the solid carburizer will introduce negligible nitrogen contents into the case. Thus a basis is at hand for comparison of the effect of nitrogen on case hardness.

In determining the carbon and nitrogen gradation through the case, the large diameter rounds were held in the liquid baths for periods of 10, 30 and 120 minutes at a temperature of 1470 degrees Fahr. (798 degrees Cent.) for the carbon-chromium steel and 1500

degrees Fahr. (815 degrees Cent.) for the nickel-chromium steel. The samples were slowly cooled in lime upon removal from the baths to facilitate removal of chips in machining off the case.

The determination of the carbon and nitrogen content was accomplished by removal of successive layers of 0.004, 0.004 and 0.010 inches from the radius along a 5-inch length. The series of chips thus removed were analyzed for carbon and nitrogen content.

In determining nitrogen a weighed amount of chips is dissolved in 1:4 sulphuric acid. The solution thus formed is slowly admitted by a dropping funnel into a boiling solution of sodium hydroxide contained in a Kjehldahl flask. Ammonia formed by decomposition of the nitrides present is distilled off. The distillate is then titrated hot with .01N sodium hydroxide and nitrogen content calculated.

The small diameter samples intended for hardness determinations were treated in the following manner:

Steel	Time in bath	Quench
Nickel-chromium	10 minutes at 1500 degrees Fahr. (815 degrees Cent.)	Oil
Carbon-chromium	10 minutes at 1470 degrees Fahr. (798 degrees Cent.)	Oil
Nickel-chromium	30 minutes at 1500 degrees Fahr.	Oil
Carbon-chromium	30 minutes at 1470 degrees Fahr.	Oil
Nickel-chromium	2 hours at 1500 degrees Fahr.	Oil
Carbon-chromium	2 hours at 1470 degrees Fahr.	Oil

Samples for treatment in these liquid hardening baths were submitted to the companies making these compounds and were carburized and quenched in their laboratories. The solid pack carburizing treatment using Compound No. 5 was done at the Republic Steel Corp. metallurgical laboratory by carburizing both the large and small diameter samples for a 5-hour period at 1500 degrees Fahr. (815 degrees Cent.).

The small hardness samples were returned in the as quenched condition. One series of samples was retained in this condition while the other sets were drawn in the following manner:

300 degrees Fahr. (150 degrees Cent.) draw—Oil bath—½ hour at temperature
350 degrees Fahr. (176 degrees Cent.) draw—Oil bath—½ hour at temperature
400 degrees Fahr. (204 degrees Cent.) draw—Oil bath—½ hour at temperature
450 degrees Fahr. (232 degrees Cent.) draw—Salt bath—½ hour at temperature
500 degrees Fahr. (260 degrees Cent.) draw—Salt bath—½ hour at temperature
500 degrees Fahr. (288 degrees Cent.) draw—Salt bath—½ hour at temperature
600 degrees Fahr. (316 degrees Cent.) draw—Salt bath—½ hour at temperature

A series of hardness readings were taken on one flat surface of the prepared hardness samples, starting on the original surface and

then at successive intervals of several thousandths of an inch below the surface on the samples treated 10, 30 and 120 minutes in the various baths.

Another series of hardness readings were taken along a 3-degree taper grind through the case and into the core, the purpose of which was to obtain a series of hardness values from the extreme surface and well into the core to show the hardness gradation. Readings taken in this manner were only made on samples treated for a 2-hour period, and were made on single samples. Several series of readings were made through the case of each taper ground sample for comparison of reproducibility of results.

All hardness determinations were made with a Vickers Brinell pyramidal diamond hardness testing machine using a 10-kilogram load. The 3-degree taper ground samples were mounted in a special jig which permitted a series of evenly spaced readings to be taken through the case and into the core.

Discussion of Results

The results of this investigation will be considered with regard to the carbon and nitrogen gradation through the case; the flat surface hardness; metallographic examination and the taper ground gradation hardness.

A consideration of the carbon and nitrogen gradation through case (Table II), developed by the various treatments, shows generally a high value of nitrogen in the first cut (surface to 0.004 inch). This is more typical of the nitrogen, however, than the carbon penetration. There is a definite tendency for a higher concentration of carbon in the surface cut which can be evaluated by comparison of the difference in carbon content between the second and third cut as compared with the difference between the first and second cut. This difference is more evident on studying the data obtained for Baths Nos. 3 and 4 and the solid carburizer (Compound No. 5) which introduce a higher carbon content into the case than Baths Nos. 1 and 2. Generally the carbon-chromium steel was found to contain a higher carbon content in the case; however, this steel contained somewhat more carbon to start with (see Table I) than the nickel-chromium so this result is to be expected. Baths Nos. 1, 3 and 4 showed the nickel-chromium steel to have the higher nitrogen content in the

case as compared with the carbon-chromium steel. The highest nitrogen content was present in samples treated in Bath No. 2 and substantial amounts of nitrogen were introduced by Baths No. 1 and No. 4.

With regard to the concentration of nitrogen and carbon in the first cut (surface to 0.004 inch) a consideration of the carburizing temperatures used will explain this phenomenon. A temperature of 1470 degrees Fahr. (800 degrees Cent.) was used for the nickel-chromium steel and 1500 degrees Fahr. for the carbon-chromium. These temperatures are just 25 degrees Fahr. higher than the upper critical points. Diffusion of these two elements is relatively slow at these temperatures and consequently they will tend to concentrate in the surface region.

Table II
Carbon and Nitrogen Determinations

Bath No.	Time in Minutes	Steel Cut	Average Depth	Carbon		Nitrogen	
				Nickel-Chromium	Carbon-Chromium	Nickel-Chromium	Carbon-Chromium
1	10	1	0.002	0.504	0.728	0.176	0.053
1	10	2	0.006	0.482	0.507	0.057	0.016
1	10	3	0.013	0.418	0.504	0.018	0.008
1	30	1	0.002	0.540	0.630	0.178	0.174
1	30	2	0.006	0.496	0.580	0.040	0.021
1	30	3	0.013	0.453	0.520	0.015	0.008
1	120	1	0.002	0.650	0.650	0.403	0.367
1	120	2	0.006	0.695	0.673	0.112	0.114
1	120	3	0.013	0.567	0.583	0.037	0.015
2	10	1	0.002	0.441	0.542	0.314	0.354
2	10	2	0.006	0.428	0.504	0.050	0.036
2	10	3	0.013	0.411	0.490	0.016	0.014
2	30	1	0.002	0.553	0.567	0.295	0.619
2	30	2	0.006	0.485	0.507	0.045	0.044
2	30	3	0.013	0.433	0.480	0.018	0.015
2	120	1	0.002	0.587	0.589	0.503	0.611
2	120	2	0.006	0.506	0.561	0.192	0.122
2	120	3	0.013	0.462	0.534	0.028	0.025
3	10	1	0.002	0.591	0.777	0.166	0.117
3	10	2	0.006	0.425	0.534	0.024	0.030
3	10	3	0.013	0.414	0.500	0.011	0.008
3	30	1	0.002	0.804	0.741	0.190	0.124
3	30	2	0.006	0.567	0.706	0.030	0.040
3	30	3	0.013	0.410	0.531	0.006	0.010
3	120	1	0.002	0.870	0.927	0.110	0.120
3	120	2	0.006	0.722	0.709	0.058	0.043
3	120	3	0.013	0.620	0.600	0.020	0.017
4	10	1	0.002	0.668	0.591	0.147	0.042
4	10	2	0.006	0.548	0.500	0.051	0.010
4	10	3	0.013	0.416	0.496	0.015	0.006
4	30	1	0.002	0.800	0.728	0.156	0.097
4	30	2	0.006	0.504	0.619	0.027	0.046
4	30	3	0.013	0.428	0.507	0.019	0.024
4	120	1	0.002	1.49	0.951	0.268	0.244
4	120	2	0.006	0.837	0.728	0.166	0.056
4	120	3	0.013	0.640	0.567	0.033	0.012
5	300	1	0.002	1.55	1.71	0.016	0.022
5	300	2	0.006	1.07	1.175	0.017	0.018
5	300	3	0.013	0.96	1.01	0.014	0.017

METALLOGRAPHIC EXAMINATION

Metallographic examination of the samples treated 120 minutes in the various baths and 300 minutes in the solid carburizer was made on samples in the as-quenched condition and on those drawn at 600 degrees Fahr. (315 degrees Cent.). It was noted that many of the as-quenched samples showed discontinuous cementite surface skin; samples drawn at 600 degrees Fahr. (315 degrees Cent.) were examined because this condition could be more satisfactorily observed when any retained austenite in the surface cementite skin had decomposed to a dark etching tempered martensite.

The microstructures obtained by treatment in the various baths and solid carburizer showed the nickel-chromium samples to have a consistently coarse-grained case and core structure as contrasted with the finer grained structure developed by the carbon-chromium samples. This behavior is accounted for by the McQuaid-Ehn grain size which showed the nickel-chromium steel to be inherently coarse-grained and the carbon-chromium steel to be a fine-grained type. The fact that the nickel-chromium steel showed a coarse grain even at 1500 degrees Fahr. (815 degrees Cent.) indicates that it must have been an extremely coarse grain type.

All the case microstructures obtained on the nickel-chromium steels showed the formation of martensite with some retained austenite, the latter being consistently more abundant in occurrence in the coarse-grained case structures of the nickel-chromium steel. The amount of retained austenite present in the sodium cyanide treated samples was very slight. A thin cementite skin was formed on all samples except those treated in the sodium cyanide bath.

Baths Nos. 1, 3 and 4 and Compound No. 5 resulted in the formation of a martensite-austenite case structure and free cementite at the surface regardless of the type of steel. Typical structures observed are illustrated in Figs. 1 to 4.

The occurrence of the cementite skin at the surface of these case hardened samples is of considerable interest from two viewpoints. In the first place it indicates that the diffusion of carbon from the surface into the core was quite slow which is in accordance with the fact that low carburizing temperatures result in a concentration of carbon at the surface due to a low diffusion rate.

The theoretical carbon content of pure cementite, Fe_3C, is 6.67 per cent. In several instances nearly solid carbide surfaces were

Fig. 1—Detail of Case Hardened Structure Adjacent to Surface. Typical of Nickel-Chromium Steels Treated in All Baths Except No. 2 (Sodium Cyanide). Nital. × 1000.
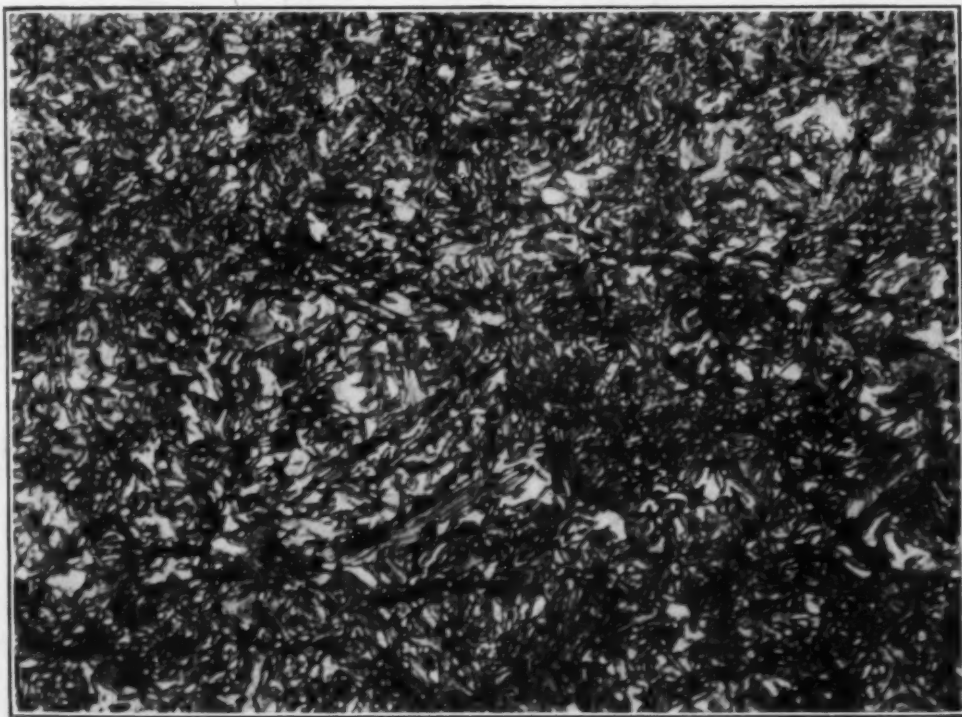

Fig. 2—Detail of Case Hardened Structure Adjacent to Surface. Typical of Carbon-Chromium Steels Treated in All Baths Except No. 2. Nital. × 1000.
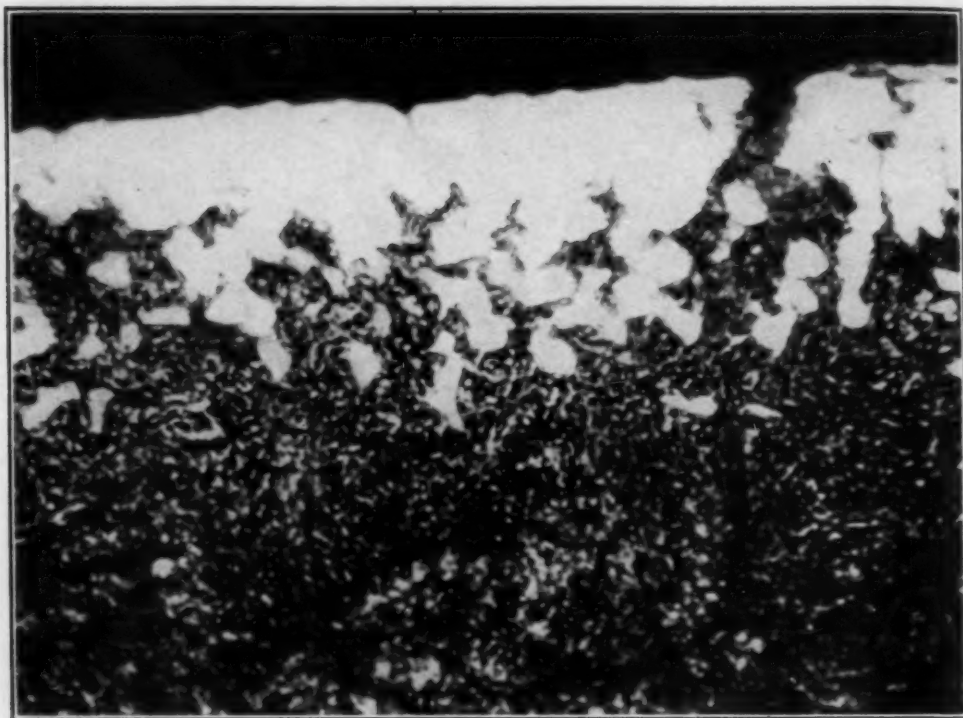
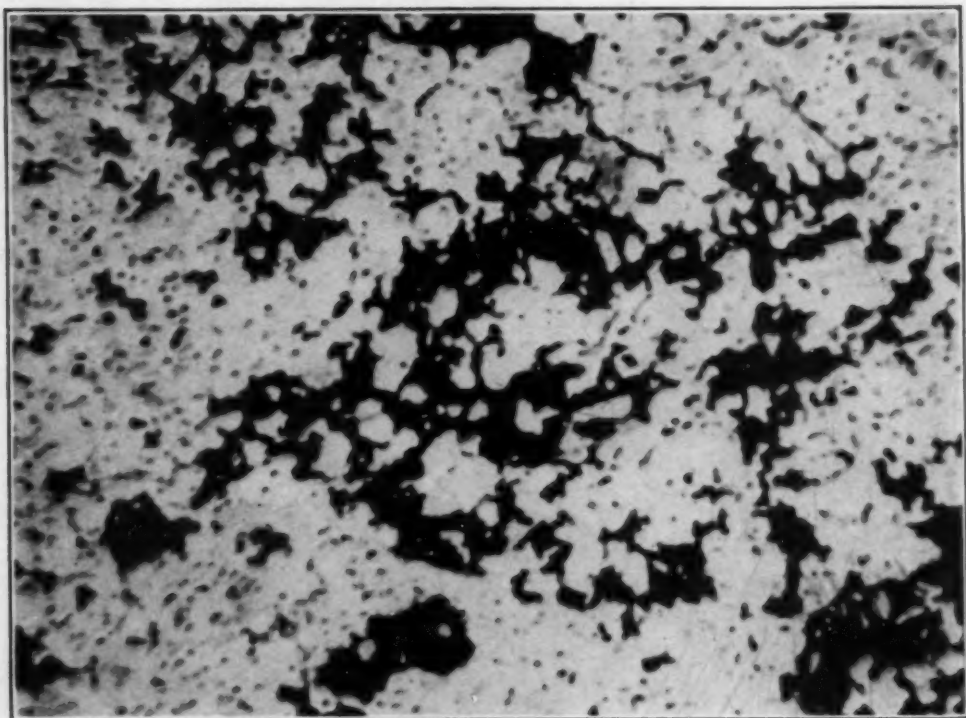Fig. 3—Appearance of Carbide Segregation at Surface. Transverse Section. Nital. × 1000.

Fig. 4—Appearance of Carbide Segregation on Surface. Polished Directly on Surface. Nital. × 1000.

noted on the samples which would indicate actual surface carbon contents of the order of at least 4.5 per cent up to 6.0 per cent. At this point it can be stated that carbon checks run on successive cuts taken from the surface of a large diameter round give an incomplete picture of the carbon diffusion and only indicate in a qualitative manner the relative degree of carbon penetration by the various methods used. That the same condition exists in regard to the nitrogen penetration is shown by chemical analysis although no direct metallographic evidence was obtained in this respect.

Previous investigations by R. W. Schlumpf[1] have shown conclusively that as the carburizing temperature is lowered a concentration of carbon occurs in the surface area. This phenomenon was particularly apparent at such low carburizing temperatures at 1500 and 1550 degrees Fahr. (815 and 845 degrees Cent.). The evidence noted in the present investigation where low carburizing temperatures were used agrees with the results of Schlumpf on the effect of carburizing temperatures on the carbon gradient.

Hardness Determinations

Flat Ground Surfaces

The data obtained on the flat surface hardness values illustrated by the typical curves in Figs 5, 6 and 7 shows the following:

Fig. 5 is that of samples treated 10 minutes. The surface hardness values for baths Nos. 3 and 4 are lower than the values determined on as quenched and subsequently drawn samples at a depth of 0.001 inch. This effect is also present with the nickel-chromium samples treated in bath No. 1. The sodium cyanide samples with highest nitrogen content in the case showed the highest hardness directly on the surface. A slight increase in surface hardness was present at the higher draw temperatures 500 and 600 degrees Fahr. (260 and 315 degrees Cent.) with samples treated in baths Nos. 1 and 3.

Fig. 6 is that of samples treated 30 minutes. The most striking feature of this series of curves is the trend in hardness at the higher draw temperatures 500 to 600 degrees Fahr. (260 and 315 degrees Cent.) shown for the curves on bath Nos. 3 and 4. The surface and 0.001 inch depth curves show a well

[1]R. W. Schlumpf, "Mechanism of Carburization," American Society for Metals Handbook, 1939 Edition.

defined increase in hardness over that of the as-quenched and
subsequently drawn from 300 to 450 degrees Fahr. (150 to 230
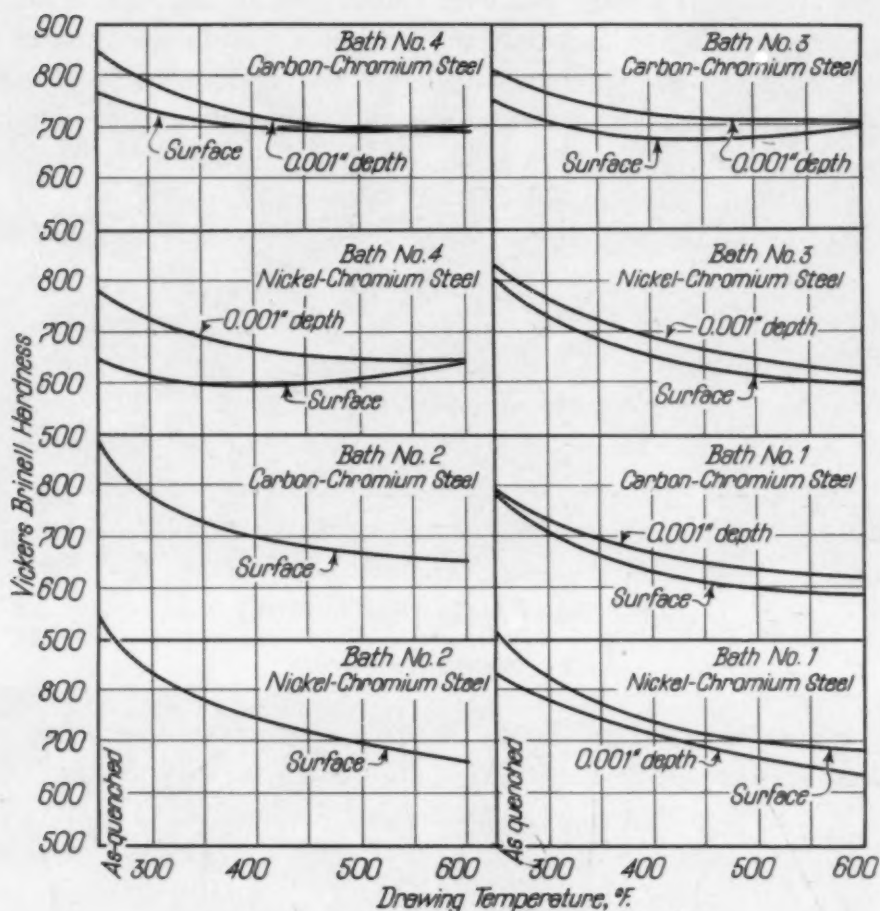degrees Cent.) hardness values. This indicates that surface

Fig. 5—Flat Ground Surface Hardness. Curves Showing Hardness on
Extreme Surface and 0.001 Inch Below. Hardness is Generally Greater at
a Depth of 0.001 Inch Except for Bath No. 2 (33 Per Cent Sodium Cyanide)
Where Maximum Hardness Occurred on the Surface.

austenite retained on quenching has transformed over to mar-
tensite, thus producing this rise in hardness. This effect is not
present on hardness curves at a depth of 0.003 inch. Bath Nos.
1 and 2 which did not introduce as high a carbon content as the
other two do not show this well defined effect.

Fig. 7 is that of samples treated for 120 minutes. The sur-
face austenite transformation phenomenon at 500 degrees Fahr.
(260 degrees Cent.) is shown up more sharply than previously.
The carbon contents of the case for samples treated in baths
Nos. 1 and 2 has increased to a point where this effect is quite

noticeable in the surface hardness curves. It is still present only in the surface and 0.001 inch depth hardness curves for samples treated in baths Nos. 3 and 4.
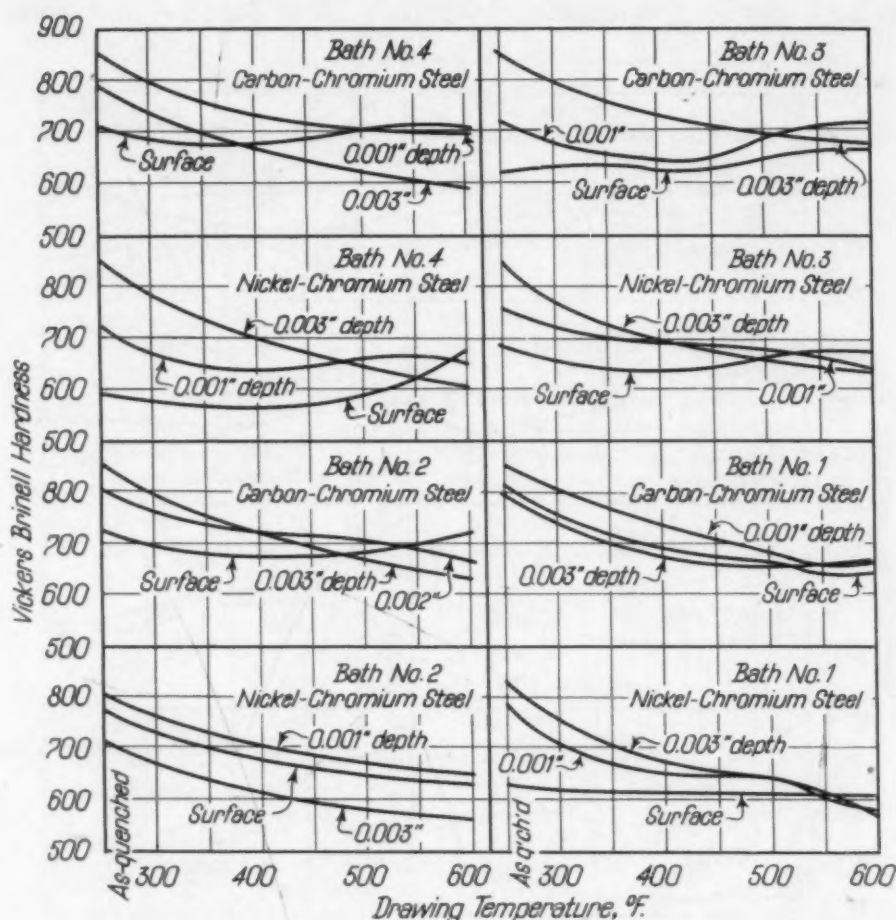

Fig. 6—Flat Ground Surface Hardness. Curves Showing a Definite Increase in Hardness on Grinding Below Extreme Surface. There is a Continuous Decrease in Hardness as the Draw Temperature Increases Except Where Large Amounts of Austenite are Present.

HARDNESS DETERMINATIONS ON 3-DEGREE TAPER GROUND SURFACES
GRADATION HARDNESS CURVES

Nickel-Chromium Steel

The hardness data obtained on the 3-degree taper ground surfaces is shown by the typical curves in Figs. 8 to 17 inclusive. These gradation hardness curves through the case show the effect of nitrogen to a greater degree than the flat surface hardness curves. The effects of nitrogen can then be more specifically discussed with this data.

In considering the effect of nitrogen on the case hardness with respect to the drawing temperature, comparisons were made first on the nickel-chromium steel between material treated in baths introducing a high nitrogen content as with Bath Nos. 2 and 4 and a low or
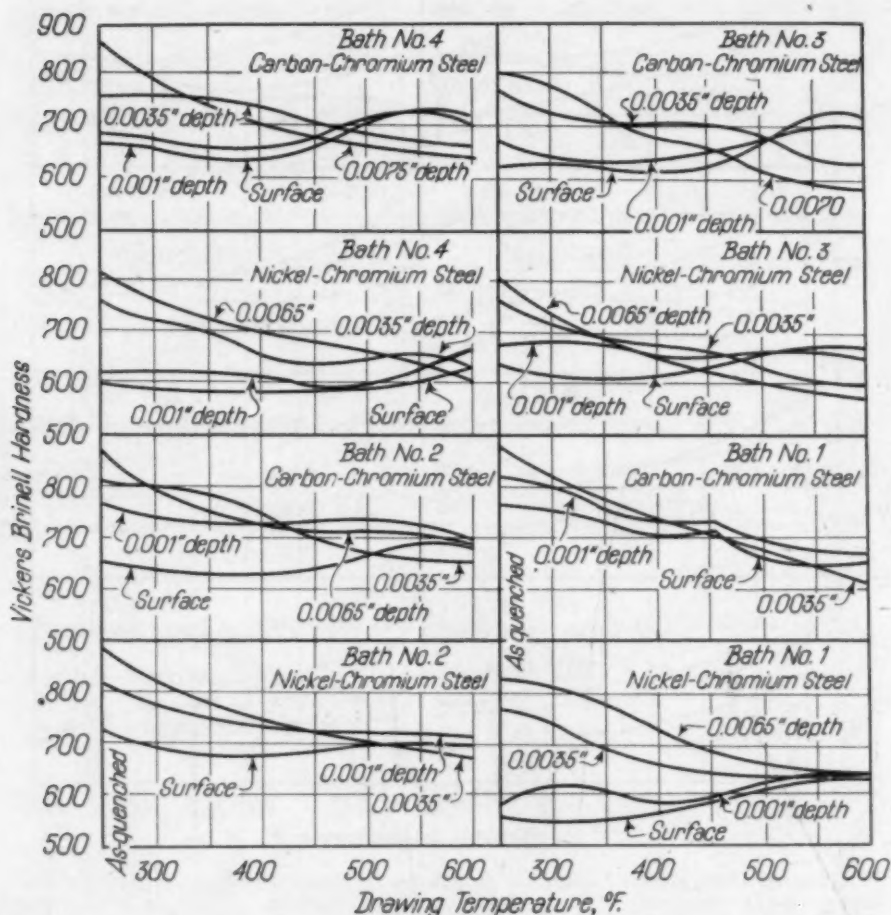

Fig. 7—Flat Ground Surface Hardness. The Retained Austenite Transformation, Starting at 450 Degrees Fahr., is Shown with Accompanying Hardness Increase at Surface and at 0.001 Inch Below. Below this Depth a Continuous Decrease in Hardness with Increasing Draw Temperature is Typical.

negligible nitrogen content as with the solid carburizer and Bath No. 3. Several specific effects were noted particularly with nickel-chromium steel.

     No. 1—Bath No. 2 (highest nitrogen) and solid carburizer (Compound No. 5—negligible nitrogen content).

     A comparison of the hardness penetration curves (Figs. 10, 16 and 12) starting from the maximum developed case hardness showed that higher drawing temperatures (at least 100
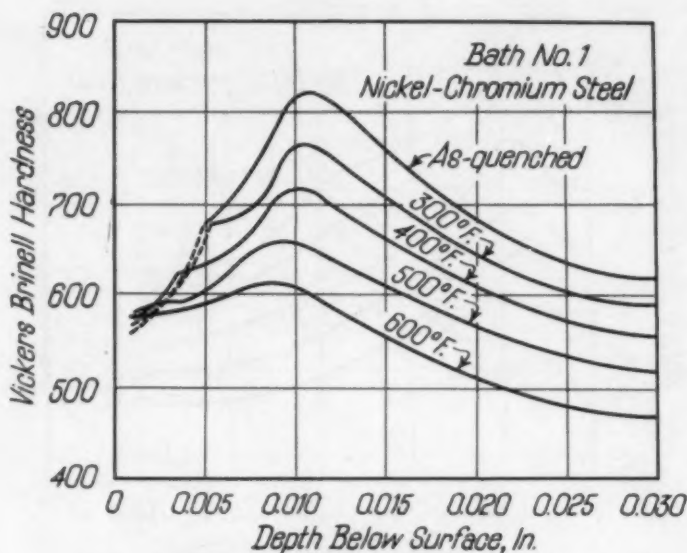
Fig. 8—Gradation Hardness Curves Through Case After 2 Hours Treatment in Bath. Curves Show the Effect of Retained Austenite on Displacing Maximum Case Hardness to a Considerable Depth Below Surface.
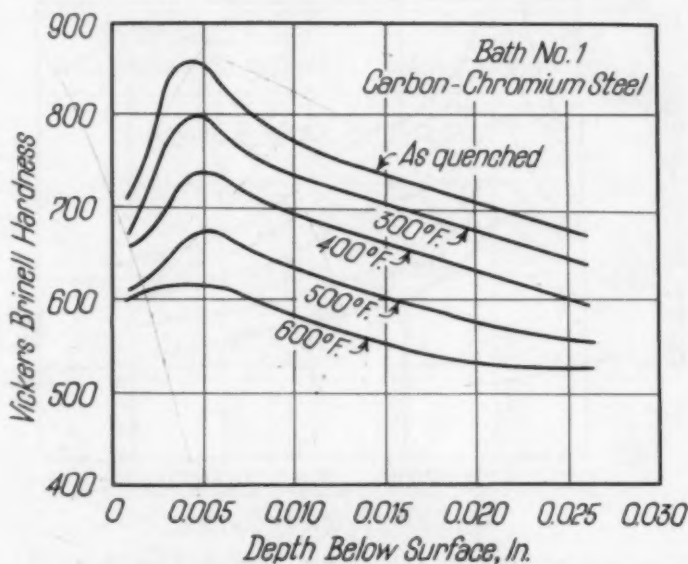
Fig. 9—Gradation Hardness Curves Through Case After 2 Hours Treatment in Bath. The Maximum Case Hardness Occurs Closer to the Surface Due to Less Retained Austenite Being Formed.

degrees Fahr. higher) would be necessary in order to obtain comparable hardness values in the high nitrogen case as compared with the solid carburized case. The effect of the high nitrogen introduced by the sodium cyanide treatment is to produce, at the various draw temperatures, a substantially higher hardness level.
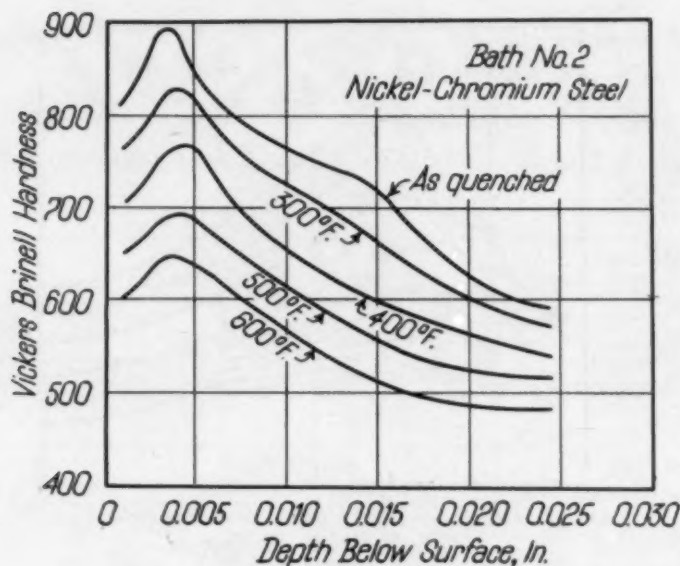
Fig. 10—Gradation Hardness Curves Through Case After 2 Hours Treatment in Bath. Maximum Case Hardness is Attained Very Close to the Surface.
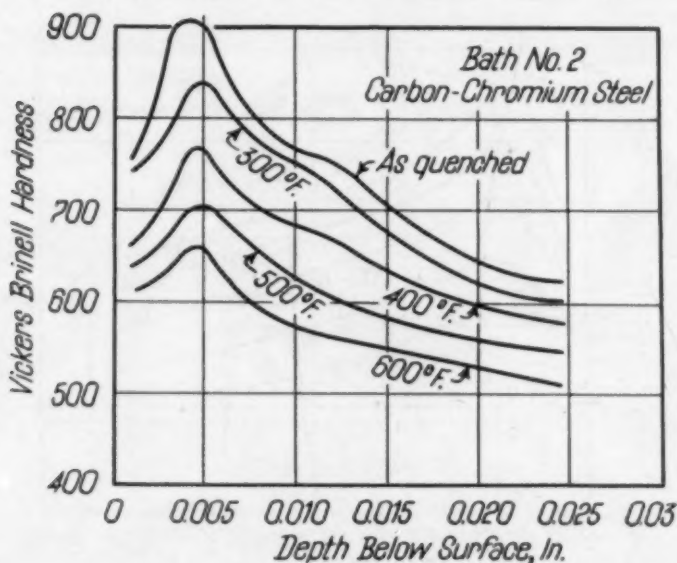

Fig. 11—Gradation Hardness Through Case After 2 Hours Treatment in Bath. The General Outline of These Curves is Essentially the Same as Shown in Fig. 10. Higher Maximum Case Hardness Values Were, However, Obtained.

No. 2—Bath No. 2 (highest nitrogen) and Bath No. 3 (low nitrogen content).

A comparison of Figs. 10 and 12 shows that in the drawn condition between 300 and 500 degrees Fahr. between the point of maximum case hardness and the core there is a definitely higher hardness level for the high nitrogen case. The low
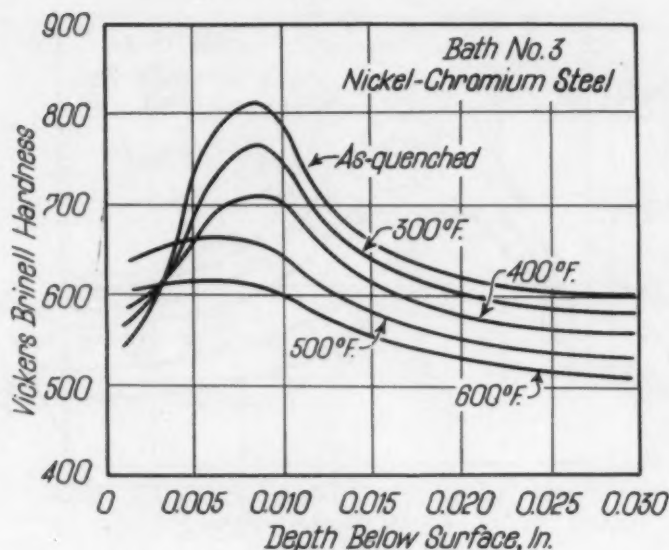
Fig. 12—Gradation Hardness Through Case After 2 Hours Treatment in Bath. A Rapid Increase in Hardness From Surface to Point of Maximum Hardness is Shown by the As-Quenched and 300 Degrees Fahr. Draw Curves.
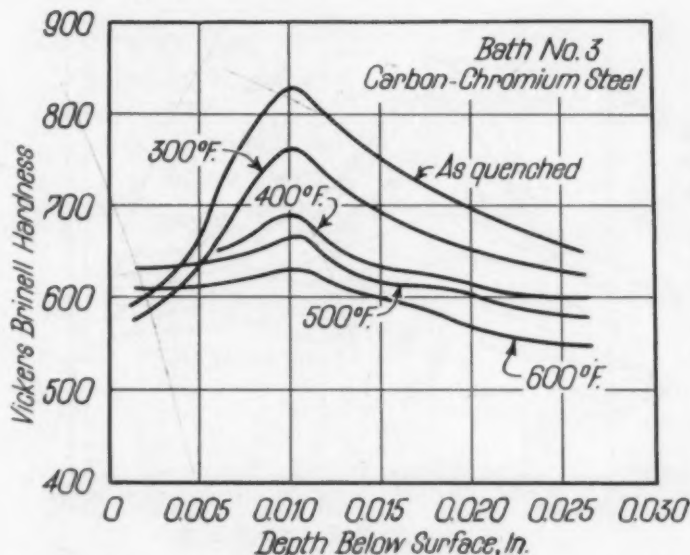

Fig. 13—Gradation Hardness Curves Through Case After 2 Hours Treatment in Bath. Substantially the Same Characteristics Are Shown by This Set of Curves as Those in Fig. 12.

nitrogen bath produced a case having a substantially higher carbon content than the sodium cyanide bath. The effect of which, on the hardness, is not significant as compared to that of nitrogen.

No. 3—Bath No. 2 (highest nitrogen content) and Bath No. 1 (medium nitrogen content).
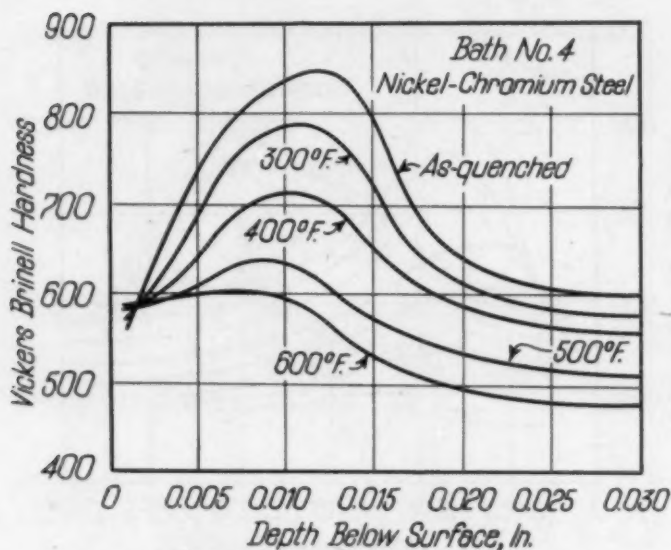
Fig. 14—Gradation Hardness Curves Through Case After 2 Hours Treatment in Bath. These Curves (Except 500 and 600 Degrees Fahr.) Show a Large and Rapid Increase in Hardness From Surface to Maximum Case Hardness Due to Retained Austenite and a Rapid Decrease From This Point to the Core.
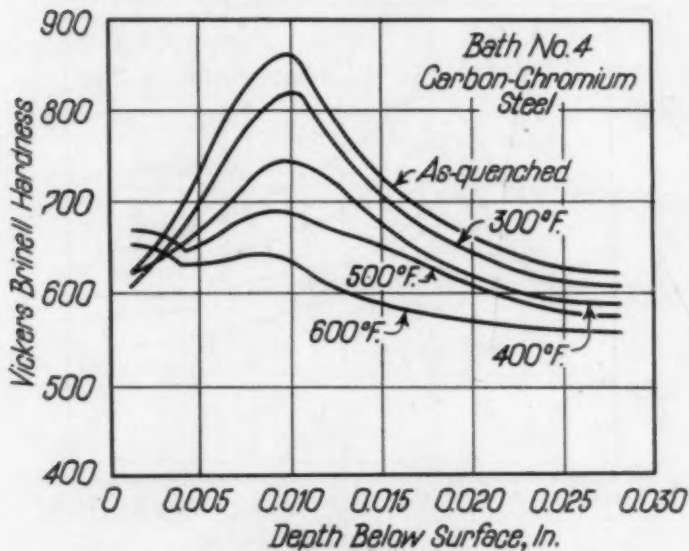
Fig. 15—Gradation Hardness Curves Through Case After 2 Hours Treatment in Bath. A Rapid Increase in Hardness is Shown From Surface to Point of Maximum Hardness on As-Quenched and 300 Degrees Fahr. Draw Curves.

This data is shown by the superimposed curves of Fig. 18 where starting from the maximum case hardness region, it is shown that the high nitrogen case developed the highest hardness. There is a distinct trend for the draw temperature curves for the Bath No. 2 treatment to maintain a higher hardness level at each draw temperature.

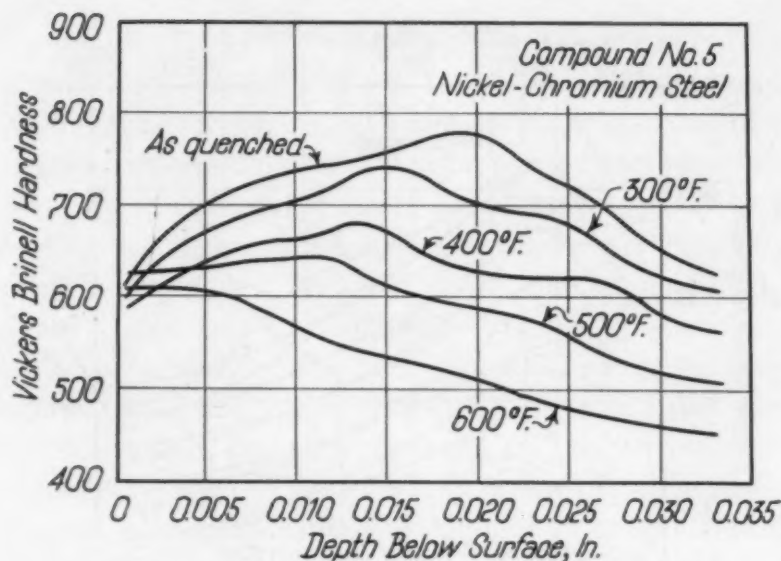Fig. 16—Gradation Hardness Curves Through Case After 5
Hours Carburizing Period. A Slow and Gradual Increase Towards
Maximum Case Hardness Values, Which Occur at a Considerable
Depth Below Surface, Appears to be Characteristic.
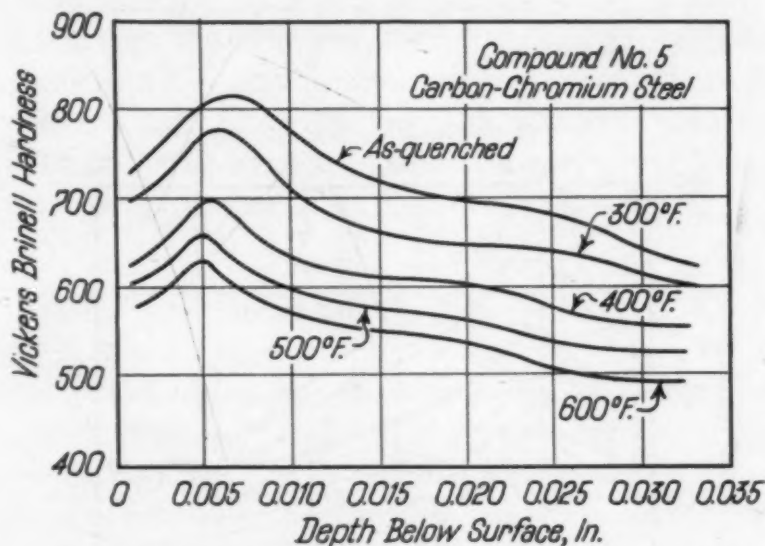
Fig. 17—Gradation Hardness Curves Through Case After 5
Hours Carburizing Period. Note Relative Position of Maximum
Hardness on This Series of Curves as Compared to Those of
Fig. 16.

No. 4—Bath No. 2 (highest nitrogen content) and Bath
No. 4 (medium nitrogen content).

Comparison of Figs. 10 and 14 show that higher hardness
values were generally obtained with the high nitrogen case. A
definitely higher hardness trend was observed particularly with
the 400, 500 and 600 degrees Fahr. curves.

Fig. 18—Gradation Hardness Curves From Above Baths
Are Superimposed From Region of Maximum Case Hardness
on Through to Core.

Fig. 19—Gradation Hardness Curves From Above
Baths Are Superimposed From Region of Maximum Case
Hardness on Through to Core. A Consistently Higher
Hardness is Maintained by the High Nitrogen Case in the
Maximum Hardness Region.

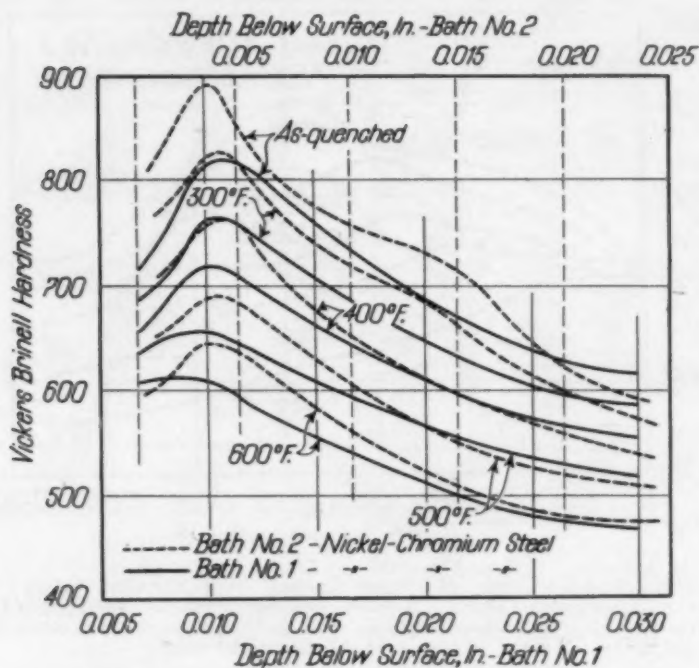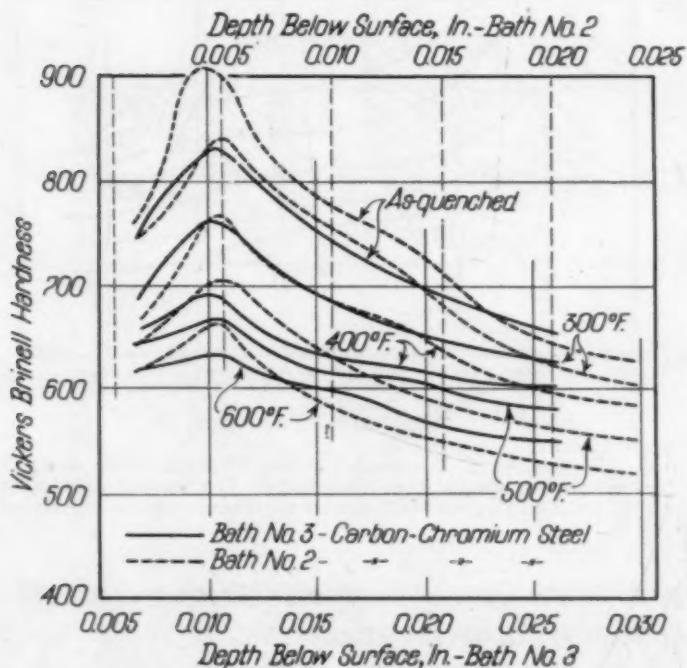No. 5—Bath No. 4 (medium nitrogen content) and solid carburizer, Compound No. 5 (negligible nitrogen content).

Comparison of Figs. 14 and 16 show that due to the sharp drop in hardness from the maximum case hardness value to the core on the curves for Bath No. 4 as compared to the more gradual hardness gradation due to the deeper case on the solid carburized samples, no satisfactory comparison of this region of the curve could be made. However, the maximum case hardness regions for the Bath No. 4 curves in the as-quenched, and quenched and drawn at 300, 400 degrees Fahr. show higher hardness values than for the solid carburized material.

Comparison between curves obtained from a medium nitrogen case content and low and negligible nitrogen content do not show very satisfactory comparison so far as the inhibiting effect of nitrogen on the hardness is concerned. This effect is shown to better advantage when there is a substantial difference in the nitrogen content. The nitrogen in the case produced by Bath No. 2 is highest and its effect is much more pronounced in comparison with low and medium nitrogen cases. The other baths generally all produced a higher carbon content than the sodium cyanide bath. Evidently the effect of nitrogen on case hardness is considerably greater than that of the carbon.

CARBON-CHROMIUM STEEL

The effect of nitrogen in inhibiting softening of the case when tempered is also brought out by the carbon-chromium steels in a manner similar to that of the nickel-chromium series.

In comparing results on hardness gradation curves obtained by the use of Bath Nos. 2 and 3 (see Fig. 19) it was noted that a general higher hardness trend was present, particularly with the 300, 400 and 500 degrees Fahr. curves for the sodium cyanide bath (No. 2).

Further comparison of the sodium cyanide curves (Fig. 11) with those obtained with the solid carburizer (Compound No. 5) Fig. 17 and Bath No. 1 (Fig. 9) again shows the inhibiting effect of nitrogen.

It was generally consistently noted that the carbon-chromium steel developed the highest maximum case hardness closer to the sur-

face than the nickel-chromium steel. This is due to the smaller amount of austenite formed on quenching.

GENERAL DISCUSSION

A consistent effect noted was that of nitrogen in inhibiting case softening during drawing in the range 300 to 600 degrees Fahr.

In regard to the highest case hardness values obtained by the various carburizing-nitriding mediums it was shown by the gradation hardness curves that the series treated in bath No. 2 (sodium cyanide) attained maximum case hardness values. No appreciable amounts of retained austenite were formed and the carbon content of the case was lower than that produced by the other carburizing mediums. Drawing in the 300 to 600 degrees Fahr. range the general case hardness level along these curves was higher than that of the other series. This effect was more pronounced with the nickel-chromium steels.

The series treated in Baths Nos. 1 and 4, both of which introduce a fairly high nitrogen content into the case did not attain the high maximum case hardness values attained by the sodium cyanide treatment in either the as quenched or subsequently drawn condition.

Comparison of the values obtained in the nitrogen bearing cases with those obtained with Bath No. 3, which reputedly produces a negligible nitrogen content in the case, and Compound No. 5 showed the case obtained by these treatments to be softer than when nitrogen is present. Bath No. 3, however, was found to introduce appreciable amounts of nitrogen which is evidently present in sufficient quantity to influence maximum case hardness because in comparison with solid pack carburizing it is seen that the Bath No. 3 values are higher. Bath No. 4 which introduces more nitrogen into the case than either Bath Nos. 1 or 3 generally shows higher maximum case hardness values in the as-quenched and quenched and drawn condition.

The factors of alloy content, inherent grain size and carbon content all affect the amount of retained austenite formed in the case. It is apparent that the carbon-chromium steel with less alloy content and an inherently finer grain size than the nickel-chromium steel consistently developed less retained austenite in the case which resulted in the maximum case hardness occurring closer to the surface. With the coarse-grained, more highly alloyed nickel-chromium steel more retained austenite was formed which resulted in the maximum case hardness occurring at a greater depth below the surface.

This retained austenite formed broke down at a draw tempera-
ture in the range 450 to 500 degrees Fahr. which resulted in an
actual increase in the extreme surface hardness up to a depth of 0.005
inch as compared with surface region hardness values in the as-
quenched, and quenched and drawn below 450 degrees Fahr. It was
noted that this transformation effect is more pronounced with nickel-
chromium steel samples treated in straight carburizing medium where
a higher carbon content is introduced into the case and more austenite
is formed.

It is of interest to note that surface hardness readings were not
affected by the thin skin of cementite formed on surface of some of
the samples. In many cases this skin was discontinuous and the
actual thickness quite small, some 0.00025 to 0.00050 inch, as meas-
ured on samples treated in Bath No. 4.

One practical application is indicated by hardness determinations
made at different depths on the flat samples in that the as-quenched
and subsequently drawn from 300 to 400 degrees Fahr. series, wear-
ing of the surface to the depth of a few thousandths of an inch
would have to occur before the abrasion resisting qualities of the
case hardened material is fully developed. With the sodium cyanide
treated material where no austenite layer is formed maximum hard-
ness is obtained in the surface area.

From the standpoint of automotive gears the sodium cyanide
bath represents the best treatment because of the high hardness
developed at the extreme surface. The carbon-chromium steel is
generally superior to the nickel-chromium steel so far as surface hard-
ness is concerned which is due to formation of less retained austenite.

As was previously mentioned, the factor of high surface hard-
ness is of special importance in the modern rigidly mounted trans-
mission due to the fact that wear of a few thousandths of an inch
will affect the performance adversely.

A statement of the conclusions to be drawn from this investiga-
tion are as follows:

(1)   A sodium cyanide bath will give the best results inso-
far as high surface case hardness is concerned.

(2)   The carbon-chromium steel was found to be gener-
ally superior to the nickel-chromium steel as regards maximum
surface case hardness. The maximum hardness occurred at a
lesser depth below the surface than with the nickel-chromium
steel due to less retained austenite.

(3)   It was found that with a medium carbon nickel-chromium steel the effect of the nitrogen content is to inhibit the softening effect on the case upon drawing in the temperature range 300 to 600 degrees Fahr. This effect was also indicated with a carbon-chromium steel.

(4)   From the standpoint of automotive gears the sodium cyanide bath is the best. (Results on Bath No. 1).

(5)   The temperature range for the decomposition of retained surface austenite was found to be 450 to 500 degrees Fahr. The retained austenite decomposition was more adequately shown by the nickel-chromium steels with high carbon contents in case.

(6)   The effect of the low carburizing temperatures used in this investigation was to produce a high concentration of carbon at the surface. This phenomenon was confirmed by chemical and metallographic methods.

(7)   Low carburizing temperatures with baths which also introduce nitrogen into the case, results in a surface concentration of nitrogen, similar to that of carbon. Nitrogen concentration at the surface was more apparent with the 10 and 30 minute treatments.

(8)   For those treatments in which a large amount of retained austenite was produced, wear of several thousandths of an inch would have to be accomplished before the maximum case hardness is attained.

AKNOWLEDGMENTS

DISCUSSION

Written Discussion: By G. Meldrum, assistant laboratory director, Metallurgical Laboratory, Republic Steel Corp., Canton, Ohio.

The present paper presents an investigation concerned largely with hardness gradation studies made on samples treated for two hours in various case

hardening baths. In many commercial applications this would be considered too long a period, particularly where thin sections are being treated. This should be taken into consideration when studying the gradation hardness curves presented.

Other case hardening baths which produce substantially higher nitrogen contents than those involved in the present investigation should be worth investigation along the lines presented.

Oral Discussion

M. F. JUDKINS:[2] I realize that the comment I have to make is perhaps beyond the scope of the present paper, but it would seem that a very interesting correlation could be drawn between the effect of nitrogen upon case hardness, and the ease of machining of the automotive gears which are commonly made from this type of steel, with regard to possible effects upon distortion and particularly relative to resistance to pitting, or surface fatigue, or the wear of the gears.

We are all prone to talk about the things that are most interesting to us, and to me the machining and the service characteristics of these automotive gears are of prime interest because that is the service to which these steels are put.

Author's Reply

In answer to Mr. Meldrum's query as to the time period utilized in treating the samples from which gradation hardness curves were plotted it was found to be necessary to use a 2-hour period. The case obtained with this treatment was sufficiently deep (0.015 to 0.020 inch) to enable a curve to be plotted which would adequately show the effects sought.

It is true that a 2-hour period in these various types of baths is generally beyond the scope of most commercial practice. These baths are designed for small parts, such as gears in modern typewriters which application would require a shorter period of time, possibly fifteen to thirty minutes to obtain a suitable case to insure resistance to abrasion.

Mr. Judkins remarks are of interest in regard to the effect of nitrogen versus the pitting of case hardened gears.

It was shown that nitrogen causes a definite increase in the maximum case hardness developed which does not drop as rapidly during subsequent tempering treatments as when the nitrogen content is negligible. The effect of this nitrogen addition then is to increase the case hardness which increase will reduce considerably the tendency towards pitting at points of contact on the gear teeth during service.

In conclusion I would like to say that it has been suggested by various members of the Society that work of this nature might be continued making further studies of the effects of higher nitrogen contents and with other types of commercially important alloy steels.

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[2]Chief engineer, Firth Sterling Steel Co., McKeesport, Pa.

THE ALLOYS OF MANGANESE AND COPPER

Electrical Resistance

By R. S. Dean and C. Travis Anderson

Abstract

The electrical resistance of manganese-copper alloys of 12.3-96.2 per cent manganese was determined at room temperature by the potential drop method. The alloys were hot-worked and then cold-worked to rods 0.25 inch square or round. Results of the quenched alloys show an interesting linear relationship between composition and resistance in the two ranges 10-40 per cent and 82-96 per cent manganese cold working has little effect on electrical resistance in these two ranges but causes a considerable increase in the range 50-80 per cent manganese. Up to 40 per cent manganese no difference in resistance was found between quenched and slow-cooled alloys. Between 40-90 per cent manganese resistance lowers stepwise with composition on slow cooling. The steps appear at simple atomic ratios of manganese and copper.

This suggests that on slow cooling ordered lattices has been formed the electrical resistance being a function of the particular lattice and independent of its composition. When alloys of 92-96 per cent manganese were quenched and reheated the electrical resistance showed a marked increase at 600 and 700 degrees Cent. (1290 degrees Fahr.). The resistance on slow-cooling to intermediate temperatures and quenching is about the same as for the quenched alloys. Only on slow cooling to room temperature does the resistance drop. Apparently, in the higher manganese alloys a secondary decomposition takes place on reheating. The ratio of atomic per cent of manganese to density was a linear function of weight-per cent manganese within the composition ranges 10-40 and 82-96 per cent. Changes in lattice structures suggested by the results are discussed.

Introduction

THIS paper is the first of a series dealing with the properties and structure of alloys of manganese and copper. The work described therein was undertaken to find advantageous uses for pure manganese produced by the electrolytic process developed by the Bureau of Mines, Metallurgical Division.[1, 2, 3]

The electrical resistance of manganese-copper alloys was one of the first properties to be studied because it had possible industrial importance in its own right and because the relationship of electrical resistance to composition and heat treatment gives an insight into the structure of the alloys themselves.

Preparation of the Alloys

Three groups of alloys were used in this investigation. One group was made from electrolytic manganese which was prepared several years ago and contained approximately 0.3 per cent sulphur. This manganese was desulphurized by borax in accordance with a method described in a previous publication.[4]

After desulphurizing with borax and removing the residual boron by treatment of the molten metal with manganese dioxide, the manganese used in preparing this group of alloys contained from a trace to 0.1 per cent boron.

The other two groups of alloys were prepared from electrolytic manganese made at a later date, and analysis showed that it contained not more than 0.02 per cent sulphur and 0.01 per cent iron.

All the alloys were prepared by melting the proper quantities of manganese and copper in an induction furnace, using an alundum crucible. No flux was used and the alloys were not deoxidized. They were cast in a copper chill mold in ingots ⅝ inch in diameter and about 4 inches in length.

The alloys were hot-worked to break down the structure,

[1]J. Koster and S. M. Shelton, "Electrolytic Manganese," *Engineering and Mining Journal*, Vol. 137, October 1936, p. 510.

[2]Progress Reports, Metallurgical Division, No. 13, Electrometallurgical Investigations, Bureau of Mines, Report of Investigations 3322.

[3]S. M. Shelton, M. B. Royer and A. P. Towne, "Electrolytic Manganese," Progress Reports, Metallurgical Division, No. 23, Bureau of Mines, Report of Investigations 3406.

[4]R. S. Dean, C. Travis Anderson, Cresap Moss and P. M. Ambrose, "Manganese and Its Alloys," Report of Investigations 3477, Bureau of Mines, 1939, p. 47.

quenched from a temperature just below the solidus, and cold-worked to rods. In working down the rods it was necessary to soften them when they became difficult to work by reheating to the previous temperature and quenching.

The alloys were finally cold-worked to rods 0.25 inch square or round. The first group was rolled to a square section. The last two groups were swaged round. The final amount of cold work varied slightly, the final reduction without intermediate heating and quenching being 0.40 inch to 0.250 inch in diameter.

Table I

Alloy No.	Series	Analysis		Quenching Temperature Degrees Cent.
		Mn	Cu	
H-87	I	95.7	3.9	1100
K-23	III	96.2	3.9	1100
H-88	I	93.4	6.4	1075
K-24	III	94.0	6.1	1075
H-89	I	90.5	8.4	1050
K-25	III	91.7	8.0	1050
H-90	I	89.9	9.8	1025
K-26	III	90.3	9.8	1025
H-91	I	87.2	11.9	1000
K-27	III	87.2	12.5	1000
H-92	I	84.7	15.0	975
K-28	III	85.2	14.9	975
H-93	I	82.2	17.2	950
K-29	III	82.4	17.8	950
H-94	I	79.3	20.0	925
K-30	III	80.1	20.0	925
K-31	III	75.3	23.8	900
K-19	II	70.7	29.5	850
K-18	II	64.9	34.7	850
K-17	II	61.3	38.7	850
K-16	II	55.4	44.4	850
K-15	II	50.1	49.8	850
K-32	III	49.7	50.6	850
K-14	II	45.5	54.4	850
K-33	III	41.9	57.8	850
K-34	III	35.9	64.4	850
K-35	III	31.1	69.3	850
K-36	III	24.9	27.5	850
K-37	III	20.5	79.2	850
K-38	III	12.3	87.8	850

The numbers, series, analyses, and quenching temperatures of the alloys used in this investigation are given in Table I.

The first group of alloys was heat treated in an ordinary muffle atmosphere. The last two groups were heated in an evacuated silica tube.

The electrical resistance was measured at room temperature by the potential drop method, the rod being placed on knife edges, set at various lengths. Measurements were made on several lengths of the rods to avoid errors due to nonuniformities. The measurements

were reproducible to less than 1 per cent in the range of resistance up to 200 ohms. In the very high resistance alloys reproducibility was about 5 per cent.

Electrical Resistance of Quenched Alloys

In Table II are given the experimental values of the specific electrical resistance in the various states. Fig. 1 shows graphically the change in specific electrical resistance with composition of the
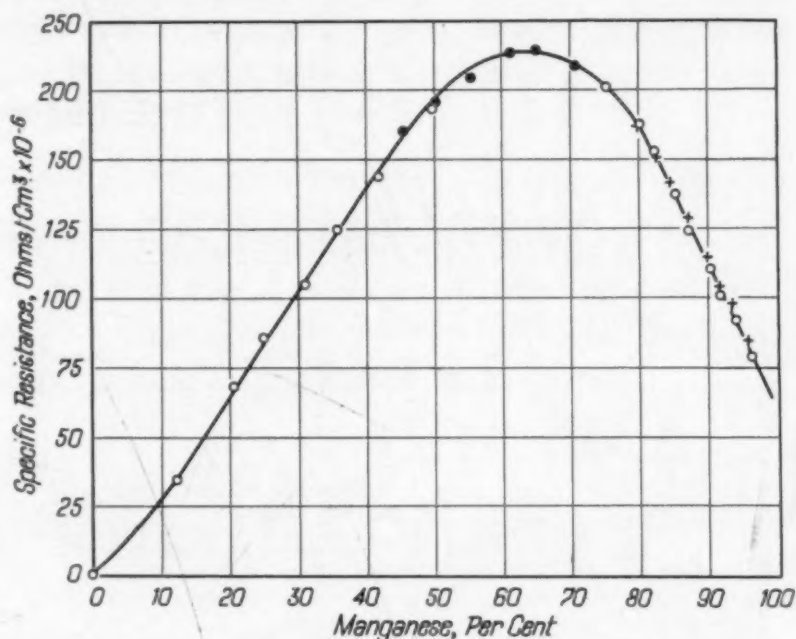
Fig. 1—Specific Resistance of Manganese-Copper Alloys in the Quenched Condition.

alloys in the quenched state. The agreement among the different alloy groups is excellent. At first glance this appears to be the resistance-composition relationship of a typical continuous series of solid solutions. However, on closer examination these results show an interesting linear relationship between composition and resistance in the two ranges of composition from 10 to 40 per cent and from 82 to 96 per cent manganese. It is unusual to find a linear relationship between weight percentage and electrical resistance, and this relationship, no doubt, results from the fact that the atomic per cent manganese divided by density is, as we shall see later, a linear function of weight percentage within the composition range under consideration.

It therefore appears that plotting weight percentage, in this

Table II

Specific Resistance $\times 10^{-6}$ Ohms

Alloy No.	Cold-Worked	Quenched	2 hours at 300°	350°	400°	450°	500°	600°	700°	800°	Slow-Cooled From Quenching Temperature
H-87	85.5	86.1	82.1				107.5	149.0			
K-23	76.9	79.3		196	332	672	890				
H-88	101.1	98.3	91.4				106.0				
K-24	89.5	92.1		109.9	119.7	139.8	161.7	274.7	407.6	497	107.2
H-89	108.0	104.3	99.8				113.5				
K-25	98.7	101.0		100.5	101.6	104.2	103.8	216.5	341.8	355	103.1
H-90	121.0	117.1	113.7				120.0				
K-26	109.8	110.8		110.5	109.6	108.6	108.0	158.5	184.2	151	103.7
H-91	132.6	129.4	123.8				123.6				
K-27	122.8	124.7		123.7	121.5	115.9	116.1	211.6	366.4	364	
H-92	147.0	141.8	136.8				128.8				
K-28	137.6	137.7		136.3	130.9	116.1	113.9	144.2	163.2	139.3	
H-93	159.0	151.1	153.1				128.5				
K-29	154.0	152.8		151.2	141.6	120.3	116.6	153.7	182.2	167.9	98.7
H-94	173.1	162.1					129.6				
K-30	164.5	162.7	162.1	161.5	146.4	121.1	117.7	157.0	205.5	205	105.4
K-31	176.9	176.4	175.5	172.9	149.2	121.9	117.2	140.6	176.6	176.7	111.9
K-19	196.5	183.9					123.0	157.6	183.7	186.4	113.7
K-18	199.0	189.2					127.2	163.5	187.8	188.5	127.6
K-17	197.7	188.2					134.6	168.8	189.9	193.5	128.9
K-16	187.5	179.3					136.4	165.3	181.0	185.2	137.0
K-15	172.5	170.4					137.6	160.0	171.4	173.1	133.6
K-32	170.0	168.5	166.2	160.8	140.9	134.1	131.7	148.9	167.9	167.5	
K-14	164.2	160.0					142.3	154.3	159.6	162.7	135.4
K-33	145.2	143.8	143.2	139.9	132.2	130.8	129.6	139.1	142.9	143.4	
K-34	126.1	124.7	123.9	123.7	121.5	121.0	120.7	123.0	122.9	124.4	102.9
K-35	105.7	104.6	103.8	104.1	104.1	103.7	103.9	103.5	103.9	103.8	
K-36	86.8	85.8	85.7	85.1	86.1	86.2	85.8	85.3	85.2	85.7	
K-37	68.7	68.2	67.6	68.1	68.3	68.4	68.3	67.8	68.2	67.2	
K-38	35.2	34.7	34.8	35.0	35.0	35.1	34.7	34.5	34.2	34.6	33.5

instance, is merely a convenient method of showing the relationship between per cent manganese atoms by volume and electrical resistance.

One explanation of the linear nature of this relationship is that the current is carried by only one kind of atom and that the resistance is therefore increased in exactly the proportion that the volume per cent of the current carrying atom is decreased. Extrapolation of the linear portions of this curve would indicate that the current carrying would pass from manganese to copper when the ratio of copper to manganese reached 1 copper : 2 manganese. Actually in the range from 50 to 60 per cent manganese both atoms seem to contribute to the conduction.

Effect of Cold Work on Electrical Resistance of Quenched Manganese-Copper Alloys

In curve A of Fig. 2, is shown the effect of cold work on the resistance of the quenched alloys shown in Fig. 1. The values plotted
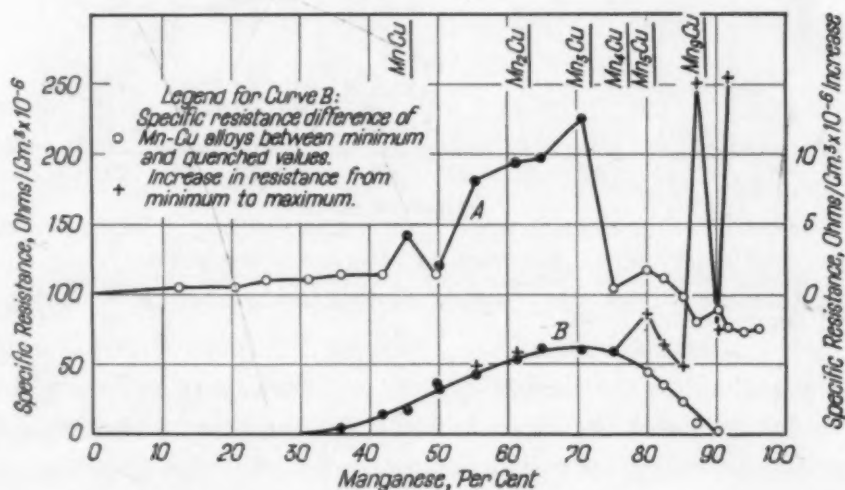

Fig. 2A—Increase in Specific Resistance of Quenched Alloys Due to Cold Work.
Fig. 2B—Specific Resistance Differences Between Minimum and Quenched Values and Increase in Resistance from Minimum to Maximum.

are the difference between the quenched and cold-worked values shown in Columns 2 and 3 of Table II. It will be seen that the compositions having a linear relationship to electrical resistance as shown in Fig. 1 are not greatly changed in resistance by cold work. The change is only a few per cent such as is noted for pure metals and simple alloys.

Up to about 50 per cent manganese cold work increases the resistance slightly. From about 50 to 80 per cent cold work brings about a considerable increase in resistance, reaching a maximum at approximately the intersection of the extrapolated linear portions of the curve in Fig. 1. The alloys, from about 80 per cent manganese up, show a decrease in the effect of cold work and from about 85 per cent manganese, the effect of cold work is negative.
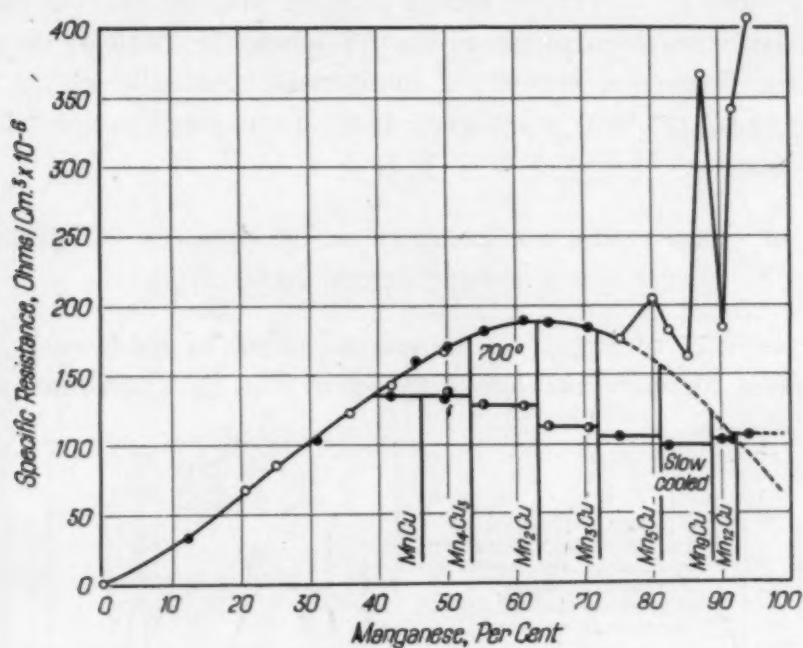

Fig. 3—Specific Resistance of Manganese-Copper Alloys After Slow Cooling in the Furnace From Just Below Solidus, and Specific Resistance of the Alloys After Quenching and Pre-heating to 700 Degrees Cent.

The probable explanation is that a tendency to ordering asserts itself to bring about the departures from linearity noted in Fig. 1. Cold work causes further disordering and makes the alloys approach the resistance indicated by extrapolation of the linear portions of the curve in Fig. 1. Whether with drastic cold work the resistance of manganese-copper alloys might be represented by two straight lines meeting at approximately 66 per cent manganese is an interesting speculation concerning which we have no further data.

ELECTRICAL RESISTANCE OF SLOW-COOLED ALLOYS

In the last column in Table II are given the values of the resistances of the alloys obtained by slow cooling in the furnace from

a temperature just below the solidus. These points are shown graphically in Fig. 3, the solid dots representing the Series II and the circles with the diagonal crosses Series III.

Up to 40 per cent manganese there is no difference in resistance between the quenched and slow-cooled alloys. Above 40 per cent manganese the resistance of all alloys up to 90 per cent manganese lower stepwise with composition on slow cooling. There is an insufficient number of alloys to permit exact placing of the steps and to determine their sharpness. The steps may be logically drawn, however, at simple atomic ratios of manganese and copper. This at once suggests that on slow cooling ordered lattices have been formed, the electrical resistance of the alloys being a function of the particular lattice and substantially independent of its composition.

More specifically we may postulate that up to an atomic ratio of nearly 1:1, the distribution remains a random one regardless of heat treatment. As a ratio of 1:1 is approached a series of ordered lattices is formed. One may suspect that free electrons are furnished in these ordered lattices entirely by a cation copper lattice and that the manganese is entering an incomplete anion lattice. On completion of this anion lattice any additional manganese atoms require formation of a new lattice. Each succeeding cation lattice is a slightly better conductor. X-ray investigations are under way that should assist in evaluating this hypothesis. When 90 per cent manganese is reached, the quenched and slow-cooled alloys have identical resistances, which may be fortuitous. With more than 90 per cent manganese, the slow-cooled lattice shows a slightly higher resistance, probably owing to a not completely suppressed secondary decomposition in the slow-cooled alloys. This secondary decomposition will be discussed later.

ELECTRICAL RESISTANCE OF QUENCHED AND REHEATED ALLOYS AND OF ALLOYS SLOW COOLED TO INTERMEDIATE TEMPERATURE AND QUENCHED

The alloys were quenched in water and, with the exception of Series I, reheated in vacuum for 2-hour periods at each successively higher temperature. When the quenched alloys are reheated to various temperatures the alloys containing 96 to 92 per cent manganese show an increase of resistance at 350 degrees Cent. (660 degrees Fahr.). This increase reaches very high values at 600 and 700

degrees Cent. (1110-1290 degrees Fahr.) and does not fall off until temperatures above 800 degrees Cent. (1470 degrees Fahr.) are reached. Other alloys, however, show either no change of resistance up to 500 degrees Cent. (930 degrees Fahr.) reheating temperature or a decrease in resistance. Above 500 degrees Cent. (930 degrees Fahr.) the resistance of all the alloys above about 30 per cent manganese increases. In alloys with more than 75 per cent manganese,
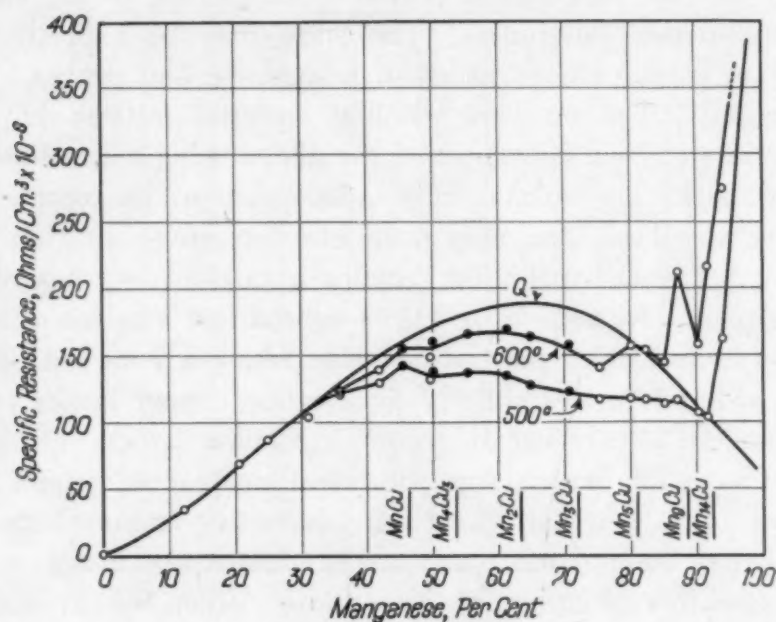

Fig. 4—Specific Resistance of Alloys Quenched From Below the Solidus and of Alloys Quenched and Reheated to 500, 600 Degrees Cent.

the increased resistance reaches a higher value than for the quenched alloys, while in alloys containing less than 75 per cent manganese, the resistance does not go above that for the quenched alloys. The resistance values obtained after quenching from the various temperatures are given in Table II. The 500, 600 degree Cent. (930, 1110 degree Fahr.) and the quenched values for comparison are shown in Fig. 4 while the values obtained after heating to 700 degrees Cent. (1290 degrees Fahr.) are shown in Fig. 3, along with the slow-cooled values and the quenched values for comparison. Fig. 2 shows that at 700 degrees, all the alloys up to 75 per cent manganese have returned to the resistance of the quenched alloys.

Figs. 5 and 6 show the effect of reheating on the specific resistance of several alloys. They also show in some instances the resistance of the same alloys, slowly cooled in the furnace. These

Table III
Specific Resistance × 10⁻⁶ Ohms of Alloys Heated to the Original Quenching
Temperature, Slow-Cooled in the Furnace and Quenched at the Various Temperatures

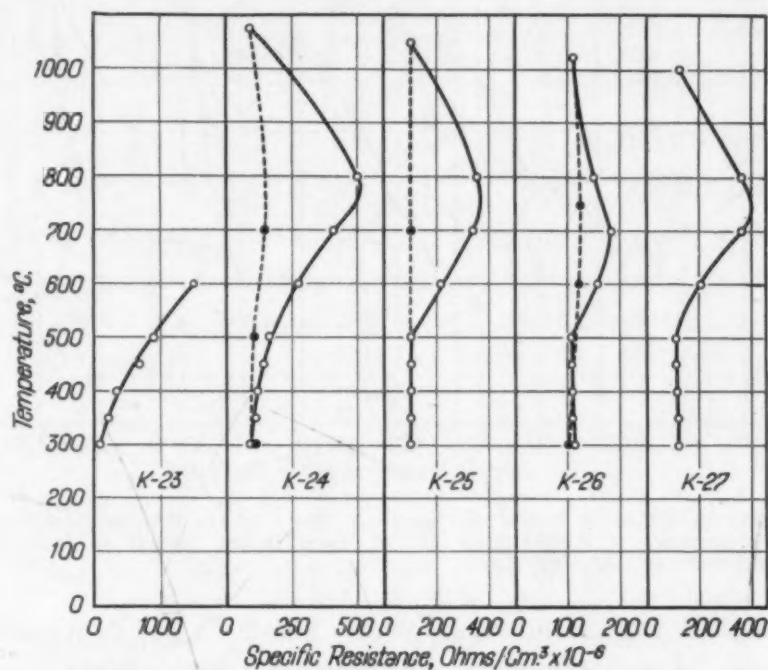| Alloy No.	Degrees Cent.			
	750	700	600	500
K-24	.....	97.7	.....	106.0
K-25	.....	103.0	.....	106.1
K-26	125.6	.....	123.6	.....
K-29	149.6	.....	140.8	.....
K-31	174.5	.....	162.9	.....

Fig. 5—Effect of Reheating Quenched Alloys on the Specific
Resistance, and Resistance of Alloys Slow Cooled From Below
Solidus to Indicated Temperature and Quenched.

are shown plotted at 300 degrees Cent. (570 degrees Fahr.). A
number of the alloys that had been slowly cooled in the furnace to
certain temperatures and quenched are also shown. The experi-
mental values obtained by this treatment are shown in Table III.

It can be seen that the resistance on slow cooling to inter-
mediate temperatures and quenching is substantially the same as for
the quenched alloys. Only on slow cooling to room temperature does
the resistance drop, and then to a point not far from the minimum
value obtained on reheating. From this, we may conclude that
ordering of the lattice takes place only on slow cooling to substan-
tially room temperature. On reheating after quenching, however,
ordering commences at 300 degrees Cent. (570 degrees Fahr.) and
is substantially complete at 500 degrees Cent. (930 degrees Fahr.).

Curve B of Fig. 2 shows that, for alloys below 75 per cent manganese, the decrease of resistance on reheating to approximately 500 degrees Cent. (930 degrees Fahr.) exactly equals the increase after heating to approximately 700 degrees Cent. (1290 degrees Fahr.). In this range, then, the processes are entirely reversible.
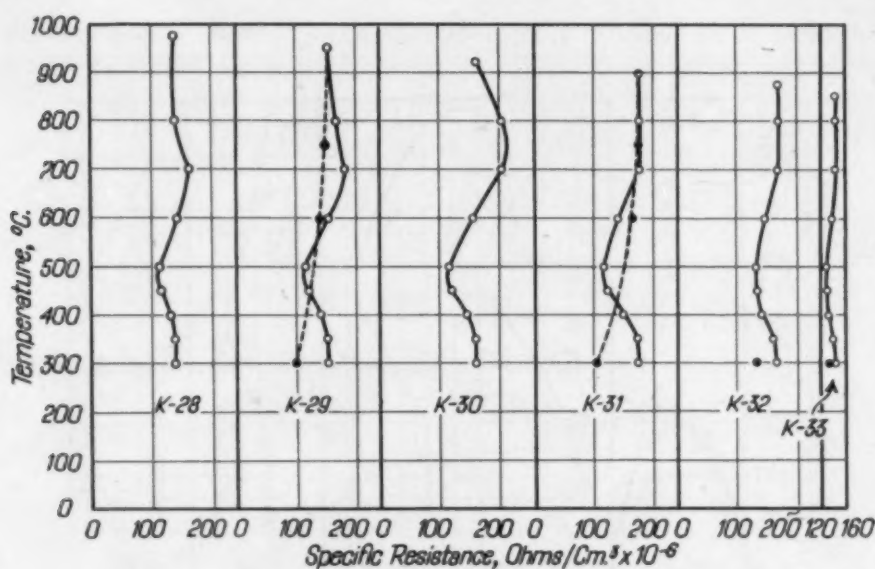

Fig. 6—Effect of Reheating Quenched Alloys on the Specific Resistance, and Resistance of Alloys Slow Cooled From Below Solidus to Indicated Temperature and Quenched.

As Curve B of Fig. 2 shows, however, above 75 per cent manganese the increase of resistance on reheating to temperatures above 500 degrees Cent. (930 degrees Fahr.) is very much greater than the decrease, which, in fact, drops to zero at 90 per cent manganese.

We conclude from this, that in the higher manganese alloys, a secondary decomposition takes place on reheating. Since no such decomposition takes place on cooling slowly, only the ordered lattice must decompose. On cooling, ordering does not take place until below the temperature at which the secondary decomposition proceeds at a finite rate. On reheating, ordering is practically complete before the secondary decomposition becomes rapid at 600 degrees Cent. (1110 degrees Fahr.).

In alloys containing more than 90 per cent manganese, as shown in Fig. 5, preliminary ordering, if present, is not indicated by a decrease in resistance on reheating. Slow cooling, however, fails to bring about decomposition so we may assume that these alloys like the others undergo preliminary ordering. The exact nature of this

secondary composition cannot be determined from electrical resistance alone. The simplest assumption is that alpha manganese is sep-

Table IV

| Alloy No.	Wt. % Mn	Atom % Mn	d	Atom % /d	Alloy No.	Wt. % Mn	Atom % Mn	d	Atom % /d
H-87	95.7	96.3	7.13	13.51	K-30	80.1	82.3	7.03	11.70
K-23	96.2	96.7	7.16	13.50	K-31	75.3	78.0	7.03	11.09
H-88	93.4	94.3	7.06	13.36	K-19	70.7	73.7	7.08	10.41
K-24	94.0	94.8	7.09	13.37	K-18	64.9	68.2	7.05	9.67
H-89	90.5	91.7	7.15	12.82	K-17	61.3	65.2	7.10	9.18
K-25	91.7	92.7	7.10	13.06	K-16	55.4	58.4	7.20	8.11
H-90	89.9	91.2	7.03	12.97	K-15	50.1	53.7	7.27	7.39
K-26	90.3	91.5	7.10	12.88	K-32	49.7	53.3	7.32	7.28
H-91	87.2	88.7	7.13	12.43	K-14	45.5	49.1	7.38	6.65
K-27	87.2	88.7	7.06	12.56	K-33	41.9	45.5	7.50	6.07
H-92	84.7	86.5	7.06	12.25	K-34	35.9	39.3	7.62	5.16
K-28	85.2	87.0	7.04	12.36	K-35	31.1	34.3	7.72	4.45
H-93	82.2	84.2	7.02	11.99	K-36	24.9	27.7	7.90	3.50
K-29	82.4	84.4	7.00	12.05	K-37	20.5	23.0	8.05	2.86
H-94	79.3	81.6	6.98	11.68	K-38	12.3	14.0	8.47	1.65
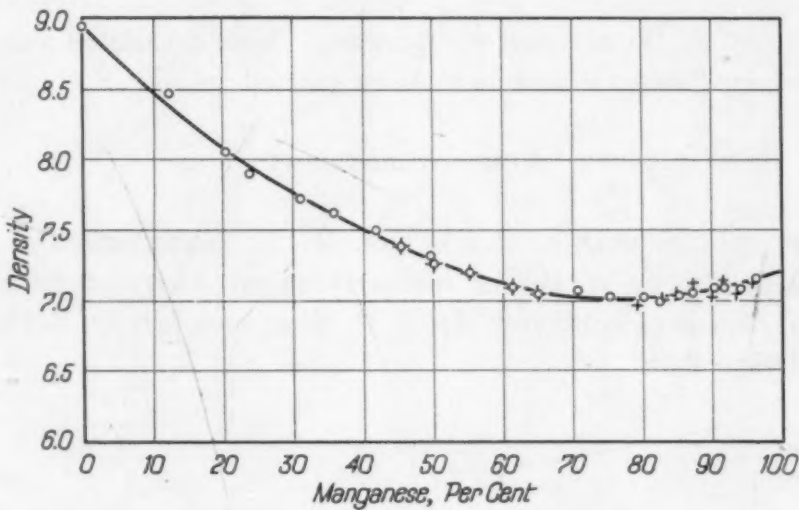
Fig. 7—Density of Manganese-Copper Alloys.

arating. This does not explain, however, the serrated resistance-composition curves shown in Figs. 3 and 4.

DENSITY OF MANGANESE-COPPER ALLOYS

In Table IV are given the experimental values of the densities of the alloys. These results are shown graphically in Fig. 7.

We have previously referred to the fact that in the quenched alloys the relationship of composition to density was such that the ratio of atomic per cent of manganese to density was a linear function of weight-per cent manganese within the composition ranges 10-40
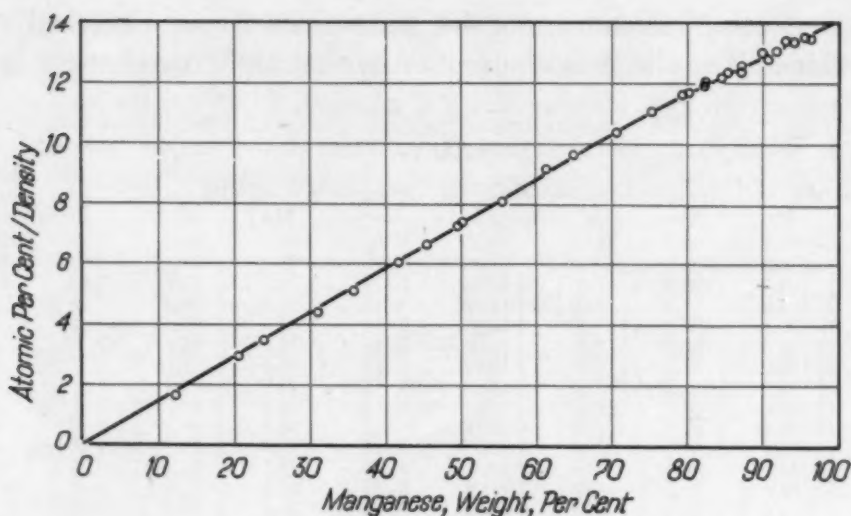
Fig. 8—Relationship of Atomic Per Cent/Density to Weight Per Cent of Manganese.

per cent and 82-96 per cent manganese. These calculated values are tabulated in Table IV and have been plotted in Fig. 8.

ACKNOWLEDGMENT

The authors wish to thank Drs. V. H. Gottschalk and E. V. Potter and Mr. F. M. Bower for carrying out many of the various electrical measurements, and Mr. J. P. Riott and Mr. D. Schlain for the analytical data.

SUMMARY

In a previous publication, we have reviewed the literature on the subject of electrical resistance of manganese-copper alloys. The values we have reported here are considerably different, owing to purity of the alloys and control of the heat treatment. By extrapolation of our results, we get a value for the specific resistance of gamma manganese of 62 michroms per cm.[3] This is higher than the calculated value of 28 michroms per cm.[3], given by Valentiner and Becker,[5] but in view of the linear extrapolation we regard our value as more accurate.

From the standpoint of practical use these alloys are principally interesting because of their very high resistances. The quenched

[5]S. Valentiner and G. Becker, "Susceptibility and Electrical Conductivity of Copper Manganese Alloys," *Z. Physik*, Vol. 80, 1933, p. 735-44.

alloys offer high resistances and low temperature coefficients. Certain ternary alloys of manganese, copper, and nickel, which will be discussed in a later paper, seem to offer certain advantages in this field, however.

The very high resistance developed in reheated alloys high in manganese is a new phenomenon that has interesting practical possibilities. The temperature coefficient of these very high resistance alloys falls as the resistance increases and is about 1×10^{-4} ohms per ohm per degree Cent. with resistance of 1000 microhms per cm.[3]

THE ALLOYS OF MANGANESE AND COPPER

Hardening by Cold Work and Heat Treatment

By R. S. Dean and C. Travis Anderson

Abstract

The effect of heat treatment and cold work on the hardness of copper-manganese alloys of 12.3-96.2 per cent manganese is discussed.

The quenched alloys increase in hardness with manganese content. High-manganese alloys harden very slowly with cold work, high-copper alloys much more rapidly. Heat treatment has little effect upon alloys containing less than 40 per cent manganese. Alloys of 40-75 per cent manganese begin to harden at 450 degrees Cent., reach maximum hardness at 500 degrees Cent., and soften progressively from 500 to 800 degrees Cent. Above 75 per cent manganese the alloys behave quite differently toward heat treatment, showing maximum hardness at 600 degrees Cent., accompanied by the separation of a second phase. Alloys containing more than 90 per cent manganese harden at a lower temperature. In high-manganese alloys the temperature and composition of maximum hardness depend upon previous heat treatment to such an extent that reproducible results are difficult to obtain. The rate of ordering may become the controlling factor in the rate and amount of hardening by precipitation.

HARDNESS OF THE QUENCHED AND QUENCHED AND COLD-WORKED ALLOYS

IN previous papers of this series we have reported data on the electrical resistance and microstructure of the manganese-copper

alloys. The present paper deals with the hardness of the alloys of
this system after various mechanical and heat treatments.

The quenched alloys increase uniformly in hardness from pure
copper to pure manganese. The extrapolated value for pure manga-
nese is about Rockwell C-32.

Cold work increases the hardness of the high-copper alloys
much more rapidly than that of the high-manganese alloys. The
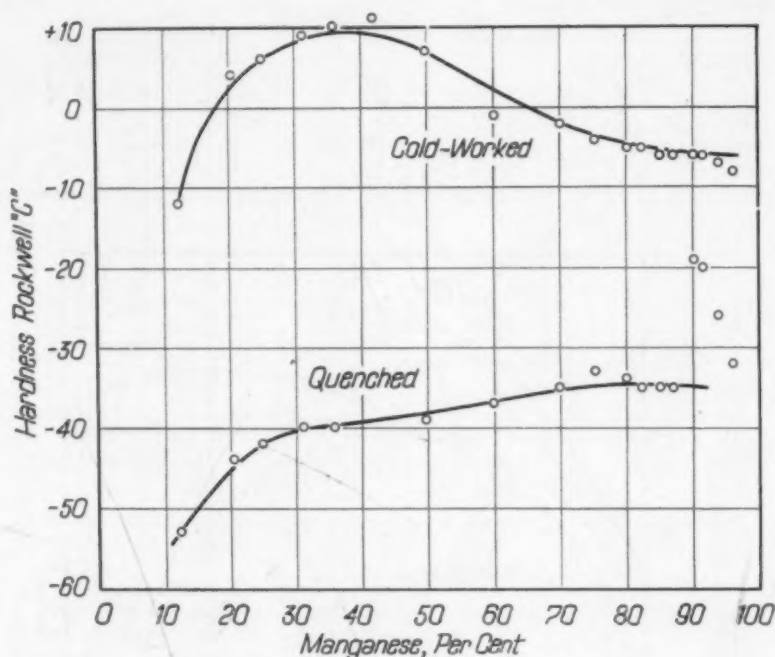
Fig. 1—Hardness of Manganese-Copper Alloys After Quench-
ing and Cold Working.

maximum of work hardening occurs at about 35 per cent copper,
the limit of the solid solution.

Alloys high in manganese harden very slowly with cold work.
Fig. 1 shows the hardness of the wrought alloys after quenching
from just under the solidus, and also the hardness of alloys cold-
worked to approximately 50 per cent reduction in area by swaging.
The plotted values are shown in Table I.

The work hardening curves for three alloys representing high-
copper and intermediate- and high-manganese alloys are shown in
Fig. 2. The alloy numbers, composition and results are tabulated in
Table II.

HARDENING BY HEAT TREATMENT

The alloys containing less than 40 per cent manganese do not
show an appreciable effect of heat treatment regardless of the tem-

Table I

Mn, Per Cent	Quenched	Cold-Worked
96.2	−32	−8
94	−26	−7
91.7	−20	−6
90.3	−19	−6
87.2	−35	−6
85.2	−35	−6
82.4	−35	−5
80.1	−34	−5
75.3	−33	−4
70	−35	−2
60	−37	−1
49.7	−39	+7
41.9	....	+11
35.9	−40	+10
31.1	−40	+9
24.9	−42	+6
20.5	−44	+4
12.3	−53	−12
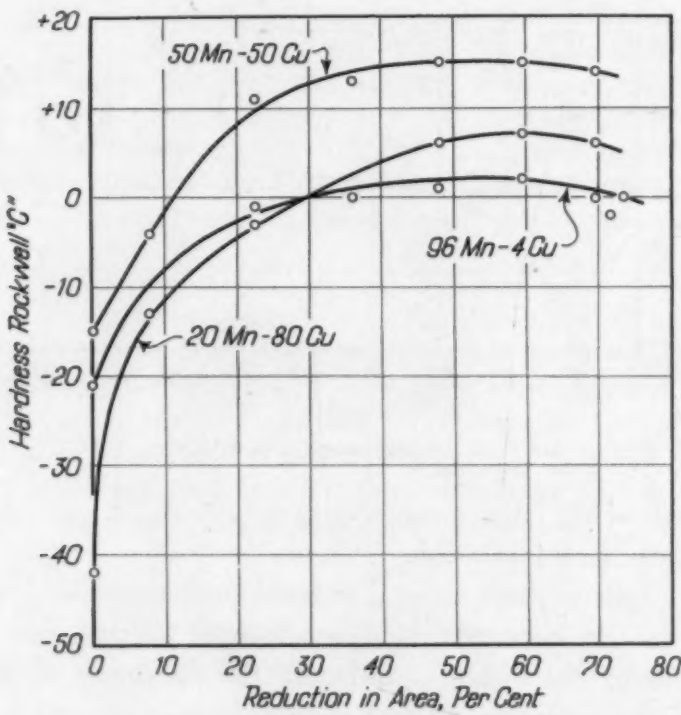
Fig. 2—Work Hardening Curve for High-Manganese, Intermediate and High-Copper Alloys.

Table II
Change of Hardness of Manganese-Copper Alloys with Reduction in Area

Alloy No.	Composition Mn	Cu	0	7.8	22.5	36.0	48.0	59.5	69.6	71.5	73.3
K-23	96	4	−21	....	−1	0	+1	−2	0	−2	0
K-97	50	50	−15	−4	+11	+13	+15	+15	+14		
K-98	20	80	−42	−13	−3	0	+6	+7	+6		

perature. Fig. 3 shows the hardness of alloys after quenching from just below the solidus and reheating to the indicated temperature for 2 hours. Alloys containing more than 40 per cent and less than 75 per cent manganese begin to harden at 450 degrees Cent. (840 degrees Fahr.) and reach a maximum hardness on heating to 500 degrees Cent. (930 degrees Fahr.). They soften progressively on
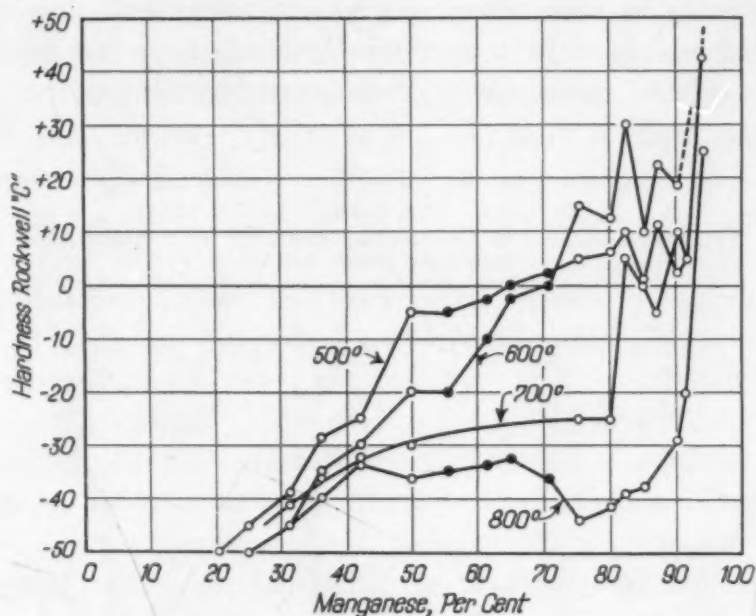

Fig. 3—Hardness of Manganese-Copper Alloys After Quench-ing and Reheating to Various Temperatures.

heating to temperatures above 500 degrees Cent. (930 degrees Fahr.) and fall to virtually their initial hardness at 800 degrees Cent. (1470 degrees Fahr.). Above 75 per cent manganese the alloys behave quite differently toward heat treatment. The 75 per cent alloy shows a maximum of hardness when reheated to 600 degrees Cent. (1110 degrees Fahr.) and a minimum when reheated to 800 degrees Cent. (1470 degrees Fahr.), which is definitely less than for the same. alloy quenched from just below the solidus (850 degrees Cent.). Alloys containing more than 75 per cent manganese show the maximum hardness after reheating to 600 degrees Cent. (1110 degrees Fahr.).

Our interpretation of the hardening of these alloys, based upon our previously reported results on electrical resistance and micro-structure, is that below 75 per cent manganese the hardening is due to the formation of an ordered lattice. Hardening by ordering of approximately this magnitude has been observed for the typical case

of ordering, copper-gold.[1] For the alloys above 75 per cent the mechanism of hardening must be more complicated. These alloys show maximum hardness at 600 degrees Cent. (1110 degrees Fahr.) and hardness is accompanied by the separation of a second phase.

In our previous paper on electrical resistance of these alloys, we have suggested that those of 90 per cent or less manganese first undergo ordering at lower temperatures and then break down to separate a second phase in a sort of Widmanstätten structure. This two-stage process can be easily demonstrated by heating the quenched

Table III

Rockwell C Hardness—Heated to Temperature Indicated for 2 Hours After Quenching from Just Below Solidus

Mn, %	Original	400° C.	500° C.	600° C.	700° C.	800° C.	900° C.
96	+2	+2	41	40	15	−9	−9
94	−12	1	34	22	41	+16	−18
92	−14	−8	29	30	45	−1	−25
90	−25	−12	11	3	33	+14	−31
87.5	−26	−10	18	31	19	−19	−29
85	−14	−21	35	34	24	−17	−29
82.5	−20	−13	34	29	13	−23	−30
80	−22	−14	30	20	2	−25	−31

alloys first to 500 degrees Cent. (930 degrees Fahr.) for 2 hours and then to 600 degrees Cent. (1110 degrees Fahr.) for varying periods. During the 600 degrees Cent. (1110 degrees Fahr.) treatment they soften for 10 or 15 minutes, then harden considerably. This indicates that the process under way in the alloys with less than 75 per cent manganese is also going on in alloys above this percentage, but that at 600 degrees Cent. (1110 degrees Fahr.) another process takes place, which brings about maximum hardening at 600 degrees Cent. (1110 degrees Fahr.).

In alloys containing more than 90 per cent manganese the hardening, which involves phase separation, takes place at a lower temperature than the homogeneous hardening. The result is very great hardening in alloys of 94 per cent manganese or more at relatively low temperatures. The hardening process in these high-manganese alloys presents some unusual features. The temperature and composition of maximum hardness depend on previous thermal heat treatment to such an extent that reproducible results are very difficult to obtain. This effect of previous treatment on hardening high-

[1]The Constitution of Gold-Copper Alloys, O. E. Harder, Metals Handbook, 1939, p. 1498.

manganese alloys is illustrated by our previously published results.[2]

Using alloys quenched from just below the solidus after 24 hours at these temperatures, Jacobs[3] obtained the results shown in Table III. It will be clear from these results that between 600 and 700 degrees Cent. (1110 and 1290 degrees Fahr.) a different hardening process has asserted itself in alloys with more than 90 per cent manganese. The hardening of the 96-per cent alloy is less at 700 than at 600 degrees Cent. (1290 and 1110 degrees Fahr.), but the 94-, 92-, and 90-per cent alloys are harder at 700 degrees Cent. (1290 degrees Fahr.). The effect of cold work on hardening in this range is also described in the Progress report referred to. It is significant that the effect of cold work on hardening at 500 degrees Cent. (930 degrees Fahr.) is quite the opposite of the usual case. Cold working definitely slows the hardening of these alloys at a given temperature. It was suggested in that publication that this effect of cold work indicated that we were dealing with ordering rather than dispersion hardening. Although the results now available indicate that a second phase is definitely separating, such separation probably will be more rapid from an ordered phase than a disordered lattice; hence, the rate of ordering may become the controlling factor in the rate and amount of hardening by precipitation.

[2]Progress Reports Met. Div. 33. "Manganese and Its Alloys," R. S. Dean, C. Travis Anderson, Cresap Moss, and P. M. Ambrose, Bureau of Mines, R. I. 3477, November 1939.

[3]J. H. Jacobs, Bureau of Mines Fellow, Missouri School of Mines, Private Communication.

THE ALLOYS OF MANGANESE-COPPER AND NICKEL

Hardening in the pseudo-binary system, Cu-MnNi

BY R. S. DEAN AND C. TRAVIS ANDERSON

Abstract

Manganese alloys with 40 to 50 per cent nickel are glass brittle. To obtain a ductile alloy 15 to 20 per cent copper must be added to an alloy of the composition MnNi. The alloys, cast in ingots ⅝ inch in diameter and 4 inches in length were swaged cold to round rods 0.25 inch in diameter with intermediate anneals at 900 degrees Cent. (1650 degrees Fahr.), and quenched from the annealing temperature. Hardness was measured by the Rockwell C scale at various stages and after heating 12 hours at 450 degrees Cent. (840 degrees Fahr.). A composition range was found in the ternary system copper-nickel-manganese where very great hardening was obtained by heating, quenching, aging treatment. Hardening may be due to the formation of the ordered lattice MnNi from the ternary solid solution. Maximum hardening was obtained by heating between 425 and 450 degrees Cent. (800-840 degrees Fahr.). Softening proceeds rapidly if the optimum hardening temperature is exceeded. The alloys are poor conductors of heat and electricity.

INTRODUCTION

THIS is the first of a series of papers reporting the properties and structures of alloys of manganese-copper and nickel. This paper reports the results on ductile alloys having a composition in the neighborhood of the pseudo-binary line Cu-MnNi that are capable of hardening by heat treatment. Later papers will consider the whole system.

The alloys of manganese and nickel from approximately 40 to

50 per cent nickel are glass brittle. Kaya and Kussman[1] have found that the ordered lattice MnNi occurs in this range, although it has no separate crystal form. We have found that to obtain a ductile alloy about 15 to 20 per cent copper must be added to an alloy of the composition MnNi.
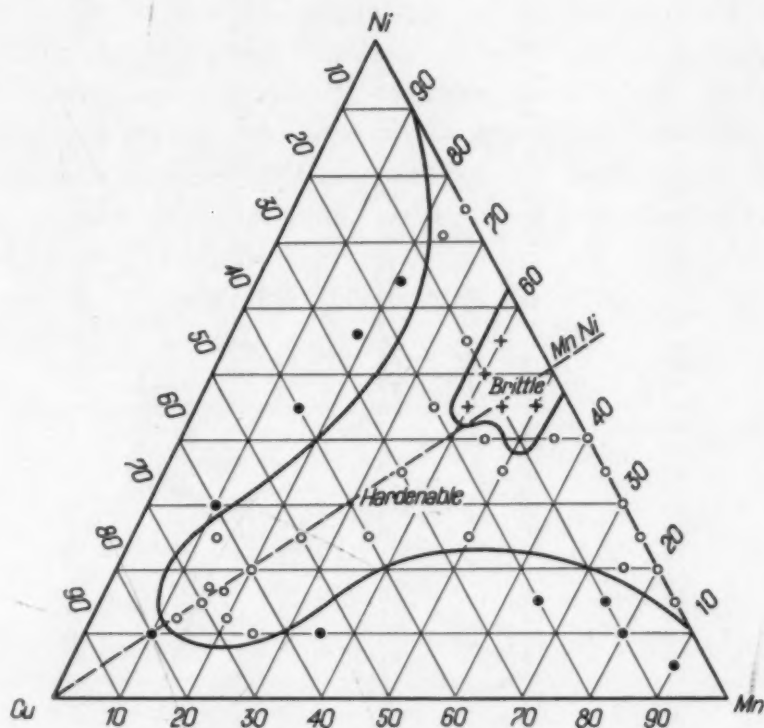
Fig. 1—The Hardenable and Brittle Areas in the Manganese-Nickel-Copper System.

PREPARATION OF THE ALLOYS

The alloys were prepared by melting electrolytic manganese, which contained not more than 0.02 per cent sulphur and 0.01 per cent iron, with electrolytic nickel and electrolytic copper in an induction furnace employing an alundum crucible. No cover, flux, or deoxidizer was used. The alloys were cast in a copper chill mold in ingots ⅝ inch in diameter and 4 inches in length. The alloys were worked down by cold-swaging with intermediate anneals at 900 degrees Cent. (1650 degrees Fahr.). They were quenched from the annealing temperature.

The alloys were finally cold-worked to round rods 0.25 inch in diameter. The final amount of cold work varied slightly, but in gen-

[1] Seiji Kaya and A. Kussman, "Ferromagnetism and the Phase State in the Binary System Nickel-Manganese", *Zeit. Physik*, Vol. 72, 1931, p. 293-309.

Table 1

Alloy Number, Composition, and Hardness After Cold-Working, Quenching, and Reheating to 450 Degrees Cent.

Alloy No.	Per Cent			CW	Q	450 degrees Cent.
	Mn	Ni	Cu			
K-39	65	35	0	25	− 6	48
K-41	65	15	20	14	−24	8
K-45	50	25	25	22	−20	29
K-46	50	35	15	24	−10	50
K-47	50	45	5		Brittle	
K-48	35	55	10	27	− 8	37
K-49	35	45	20	26	− 9	49
K-50	35	35	30	25	− 8	53
K-51	35	25	40	20	−23	48
K-53	35	10	55	16	−32	3
K-54	10	10	80	− 3	−48	−17
K-55	17	17	66	11	−41	36
K-56	10	30	60	5	−45	− 2
K-57	25	25	50	17	−26	46
K-58	15	45	40	14	−33	7
K-59	19	56	25	16	−28	6
K-60	21	64	15	20	−23	10
K-61	24	71	5	20	−15	25
K-62	25	75	0	21	−18	22
K-63	40	45	15		Brittle	
K-64	40	50	10		Brittle	
K-65	40	55	5		Brittle	
K-66	40	60	0		Brittle	
K-67	45	45	10		Brittle	
K-68	50	40	10		Brittle	
K-69	55	40	5	26	− 3	51
K-70	60	40	0	26	− 4	52
K-71	45	40	15	28	− 6	52
K-74	75	20	5	10	−12	11
K-75	75	15	10	7	−20	− 7
K-80	25	10	65	6	−42	15
K-81	20	20	60	9	−39	40
K-82	20	12½	67½	7	−40	23
K-84	15	17½	67½	5	−42	18
K-85	15	15	70	4	−42	19
K-86	12½	25	62½	4	−40	10
K-87	12½	12½	75	− 1	−44	8
K-88	70	30	0	12	−12	24
K-89	75	25	0	12	−12	18
K-90	80	20	0	9	−19	12
K-91	85	15	0	6	−21	9
K-92	80	10	10	7	−22	6
K-93	90	5	5	4	−19	0

eral the last swaging operation without intermediate annealing and quenching was from about 0.40 inch in diameter.

Hardness

The hardness of the rods was measured in the quenched state during the working-down schedule, after the final working, and after heating 12 hours at 450 degrees Cent. (840 degrees Fahr.), which was found to be close to the best hardening temperature. Some later experiments have shown that the maximum hardening is ob-

tained by heating between 425 and 450 degrees Cent. (800-840 degrees Fahr.).

The alloy number, analysis, and hardness results are shown in Table I. The area in which hardening takes place is shown in the ternary diagram, Fig. 1. A number of alloys outside this area are also included, as well as the brittle alloys. The final chemical analyses of these alloys will be given in a later paper. From previous work, it has been found that the results obtained usually vary only a few tenths of 1 per cent from the analysis calculated from the weights of the materials melted. For convenience, the Rockwell C scale was used for all the measurements, even though the hardness of the quenched alloys was negative.

The effect of reheating temperature on hardening for several alloys is shown in Table II.

Table II

| Alloy No. | Per Cent | | | Hardness Rc | | | | |
	Mn	Ni	Cu	12 hr. 350° C.	3 hr. 400° C.	3 hr. 450° C.	12 hr. 500° C.	4 hr. 550° C.
K-81	20	20	60	23	33	40	32	−21
K-82	20	12½	67½	12	14	23	− 7	−29
K-83	17	17	66	17	20	30	17	−24
K-84	15	17½	67½	13	14	18	3	−30
K-85	15	15	70	10	13	19	− 6	−39
K-87	12½	12½	75	2	3	3	−20	−38

Table III

Inches from Softened end	Hardness Rc	Inches From Softened end	Hardness Rc
3	−22	4¼	46
3½	−21	4½	47
4	− 1	5	50
4⅛	+31	6	50

It will be seen from this table that softening proceeds rapidly if the optimum hardening temperature is exceeded. The alloys are poor conductors of heat and electricity. The quantitative data on these subjects will be discussed in another paper, in which the ternary system as a whole will be considered. It will be of interest here, however, to note that the low heat conductivity permits the local softening of the hardened alloy to very sharp limits. To illustrate this, an alloy of the composition 35 per cent manganese, 35 per cent nickel, and 30 per cent copper was hardened to Rockwell C 51. A

torch was applied to approximately 4 inches of one end of the rod. Table III shows that softening was confined very sharply to the length to which the torch was applied.

Summary

A composition range has been found in the ternary system copper, nickel, manganese, where very great hardening is obtained by a heating, quenching, aging treatment. It is suggested that the hardening is due to the formation from the ternary solid solution of the ordered lattice MnNi.